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BULLETIN 606

ORIGIN OF THE ZINC AND LEAD DEPOSITS OF THE JOPLIN REGION

MISSOURI, KANSAS, AND OKLAHOMA

BY

C. E. SIEBENTHAL

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PREFACE.

By F. L. Ransome.

The author of the present report has been studying the zinc and lead deposits of the Joplin region for the last 12 years, although his work has not lain continuously in that field. His knowledge of these deposits is consequently both intimate and extensive. It is usual in presenting the results of an investigation to publish with the conclusions all the facts upon which the conclusions rest. Mr. Siebenthal has not followed this plan. Having reached definite decisions on the question of how the ores were deposited, he has deemed it best to put these decisions and the significant facts on which they are based in form for immediate publication. A full presentation of his evidence will require an account of the general geology of the region, with detailed descriptions of local tracts and individual mines. The preparation of this descriptive material, which must necessarily include many maps and illustrations, will require considerable time and some additional field work. The data will be published as a volume supplementary to the present report.

The lead and zinc deposits of the Mississippi Valley are not only of great economic importance, but have long been intensely interesting to students of ore deposits. They constitute a conspicuous example of the occurrence of sulphide ores in a region where, so far as can be determined, plutonic or volcanic activities can have had no part in their genesis.

Naturally the Joplin deposits have been much studied, and Mr. Siebenthal, on pages 39–41 of the present bulletin, has summarized the views of his predecessors, among whom have been some very able workers in economic geology. As he shows, there is not an important formation in the region that has not, at one time or another, been regarded as a source of ore constituents. Under these circumstances it was scarcely to be expected that he would add to the number of more or less reasonable hypotheses that had already been suggested or developed in explanation of the origin of these ores. His particular opportunity was that of testing these hypotheses by careful consideration of a larger body of facts than was available to earlier workers, of discovering new evidence in these facts, and, by processes of elimination, selection, and combination, of building up a consistent theory of genesis for the ore deposits of the Joplin type.

Mr. Siebenthal has succeeded well in his undertaking. In his thorough discussion of the artesian circulation, of the zinc and lead contents of the deep waters, and of the chemistry of the ore-depositing solutions he has brought new and important evidence to the support of his conclusions. Time alone can show whether these conclusions, in their entirety, are final and whether the relative effects of deposition by ascending and enrichment by descending currents have been truly estimated. But there can be no doubt that Mr. Siebenthal's careful observation and cogent reasoning have gone far to establish on a firm foundation the general conclusion that ordinary cold artesian water may under some circumstances be a very efficient agent in the solution, transportation, and deposition of the constituents of certain sulphide ores.

OUTLINE OF THE ORIGIN OF THE ZINC AND LEAD DEPOSITS OF THE JOPLIN REGION.

GEOGRAPHY.

The Joplin region is one of four metalliferous areas bordering the Ozark uplift, which is a low asymmetric dome with rudely elliptical outline, lying in southern Missouri, northern Arkansas, southeastern Kansas, and northeastern Oklahoma. The other areas are the central Missouri region, the southeastern Missouri disseminated lead region, and the northern Arkansas region.

The uplift as a whole is bounded by long, low northern and western slopes and by an abrupt southern slope. The surrounding plains have a general altitude of 500 to 750 feet above sea level. The Boston Mountains form a long, narrow plateau rising to 2,000 feet near and parallel to the southern border of the uplift. The center of the uplift has an elevation of about 1,700 feet. The St. Francis Mountains, the crystalline nucleus of the uplift, near its eastern border, also have an elevation of about 1,700 feet.

GEOLOGY.

Structurally the uplift is a broad geanticline in which the strata have no perceptible inclination except at the southern margin, where the Boston Mountains break off into a southerly dipping monocline. Superimposed upon the uplift are quaquaversal domes, of which the principal one is in the region of the St. Francis Mountains.

In the early history of the Ozark region parts of the crystalline rocks of the St. Francis Mountains were islands in an archipelago, and their erosion furnished the material that formed the Cambrian and Ordovician sandstones, which, with that which formed the associated dolomitic limestones, was spread out over Missouri and the adjacent States east, south, and west. Silurian limestones and shales were laid down on the southern and northeastern margin of the Ozark region, but apparently in all the western part of the region there was no Silurian sedimentation. During Devonian time limestone was deposited on the northern and eastern borders of the region and sandstone on the southern border. The principal Devonian formation of interest in connection with the ore deposits is the Chattanooga shale, which underlies a large triangular area in northwestern Arkansas, southwestern Missouri, and northeastern

Oklahoma. After the close of the Devonian period the Ozark region was submerged and the Mississippian limestones were laid down over probably the whole area. An elevation and a period of erosion followed, during which the limestone land developed a sinkhole or "karst" topography. This land was in turn submerged and upon its irregular, bowldery, cherty surface was laid down a series of shales and sandstones of Pennsylvanian age. It is in this basal breccia that much of the "broken" or "confused-ground" ore deposits are found. Until the close of Pennsylvanian time the crystalline area of the St. Francis Mountains was the structural and stratigraphic nucleus of the Ozark region. At the close of the Carboniferous period the Ozark region was upraised almost to its present height, the highest place coinciding closely with the geographic center. The uplifted area has since been subjected to minor warping only.

UNDERGROUND CIRCULATION.

When the covering of Pennsylvanian shale and Mississippian limestone had been eroded from the crest of the uplift the sandstones and dolomitic limestones of the Cambrian and Ordovician were exposed. As these rocks dip away on all sides and are overlain on the flanks of the uplift by impervious shale the conditions essential to artesian flow were fulfilled and an artesian circulation was consequently developed, with intake area at the central portion of the uplift, flow down the sides of the dome in sandy layers and between the limestone strata, and ascending discharge at the inner margin of the Pennsylvanian shale. As erosion removed the shale from more and more of the dome the radial artesian circulation lengthened and spread until the present conditions were established.

The quality of the water now in circulation is known from analysis of waters from deep wells, but as the water has been in circulation for a long period it must have undergone considerable change in its quality. The water in the Cambrian and Ordovician rocks beneath the Pennsylvanian shale adjacent to the uplift is largely connate and should therefore better represent that of the original circulation than does the present artesian water in the interior of the uplift. A study of the analyses of waters from the deep wells in the Pennsylvanian area bordering the uplift in Missouri, Kansas, and Oklahoma shows that they are alkaline-saline, with chlorides predominating and with high magnesium content, and that they contain free carbon dioxide and hydrogen sulphide. The original water of the Ozark circulation must have been similar. The analyses also show that the waters of many of the deep wells exterior to the uplift contain traces or weighable quantities of zinc, which precipitates as the sulphide on standing in a reservoir.

SEGREGATION OF THE ORES.

The large-quantity analyses made by J. D. Robertson show that the pre-Cambrian crystalline rocks of the St. Francis Mountains, the Cambrian and Ordovician dolomites, and the Mississippian limestone all contain notable proportions of lead, zinc, and copper. Waters charged with carbon dioxide dissolve the sulphides of the metals as bicarbonates with the evolution of hydrogen sulphide, according to this reaction:

$$ZnS + 2H_2O + 2CO_2 = Zn(HCO_3)_2 + H_2S$$

The underground water in the Cambrian and Ordovician rocks, charged with carbon dioxide, coming in contact with the disseminated sulphides, dissolved them and liberated hydrogen sulphide. The solution containing the dissolved metals and the free hydrogen sulphide moved on down the side of the dome to the inner margin of the Pennsylvanian shales, where it rose to the surface. In the open, broken cavernous ground in the Mississippian limestones at the base of the Pennsylvanian shales the solutions came nearly to rest and the carbon dioxide escaped from its union with the metals, which were precipitated as sulphides by the hydrogen sulphide yet remaining in the solution. Though this was one of the simplest and probably the chief method of solution, transportation, and deposition of the metals, they may have been carried in part as sulphates, chlorides, sulphides, hydrosulphides, or carbonates, and the zinc may have been carried as zincate or sulphozincate. The metals were in some places precipitated as carbonates or silicates by reaction with the wall rock. Some ore has doubtless been segregated from the Mississippian limestone, but for reasons stated below it is believed that the greater part of the metals was drawn from the Cambrian and Ordovician rocks.

COLLATERAL CORROBORATIVE EVIDENCE.

Items of the evidence.—In addition to the kinds of evidence set forth in some detail below the report presents several others which there is not here space to give at length, among which are the occurrence of the mining camps in a circle bordering the inner margin of the Pennsylvanian shale, the occurrence of galena and sphalerite at great depths, the general occurrence of the ore in breccias, the occurrence of galena and sphalerite in a Louisiana salt mound, and the occurrence of lead and zinc ores in the Pleasanton circle.

Reservoir sediments.—Twenty-one samples of reservoir or tank sediment deposited from waters of fifteen different deep wells, most of them in the Pennsylvanian area of Missouri, Kansas, and Oklahoma, adjacent to the Joplin region, were analyzed and zinc was found in 18 samples, lead in 17 samples, and copper in 15 samples. The following gives the average ratio of zinc to lead in the rocks analyzed by Robertson, the average ratio of zinc to lead in the reservoir samples, and the ratio of zinc to lead in the total ore mined in the Joplin region from 1907 to 1913, inclusive:

Average ratio of zinc to lead in rocks, sediments, and ores.

Pre-Cambrian crystalline rocks	1 : 0.440
Mississippian limestones	1 : 1.107
Cambrian and Ordovician dolomites	1 : 0.224
Reservoir sediments	1 : 0.211
Total ore mined from 1907 to 1913, inclusive	1 : 0.229

The thesis of this report is that the ores were derived from the Cambrian and Ordovician rocks and deposited by an ascending artesian circulation of alkaline-saline waters containing free carbon dioxide and hydrogen sulphide. The metals of the reservoir sediments were certainly so derived. The close correspondence of the ratios of zinc to lead in the Cambrian and Ordovician rocks, in the sediments and in the ores, taken together with their discrepant ratios in the crystalline rocks and in the Mississippian limestones, strongly implies the common origin of the ores and the sediments.

Four analyses were made of sediment that had accumulated in the course of a year in the reservoirs of the Pittsburg, Kans., waterworks. From these analyses it is calculated that there was deposited in these reservoirs during the year 8¼ pounds of zinc sulphide. However, this was a very small part of the zinc contained in the known total water pumped into the reservoir. According to the average of two analyses, the water contains one-half of 1 part per million of zinc. This would make a total of 1,600 pounds of zinc, equivalent to 2,400 pounds of zinc sulphide, in the water pumped in the course of a year.

Place relations of the metals.—Gottschalk and Buehler have shown that the sulphides of the metals, arranged in pairs in moistened contact, exhibit differences of electric potential, and that the mineral showing the lower potential is dissolved, while the other is unaffected. The results of their experiments throw much light on the distribution of the metals about the Ozark uplift. The nickel and cobalt ores of Missouri occur near the crystalline nucleus, and the copper ores occur along with these and also a little farther from the nucleus. The iron ores, which have been derived from sulphide deposits, occur chiefly in a circle about the crystalline nucleus. The greatest deposits of lead are not far from the nucleus, and all the central part of the uplift has produced more lead than zinc. The region that has produced more zinc than lead forms a zone around the margin of the uplift.

If the metallic sulphides are finely disseminated through the Cambrian and Ordovician limestones, particles of different sulphides must at many places be in contact. Under such conditions the ground water will dissolve first the sulphide of lowest potential, while the sulphides not in contact will go into solution in the order of their solubility. As a result, the solution of sphalerite will be greater than that of galena and the solution of both greater than that of copper, and so on through the scale. And so, if the metals have been derived from the crystalline rocks and from the Cambrian and Ordovician limestones, we should expect to find, as we do in fact find, that the copper, iron, nickel, and cobalt remain near the nucleus, that lead lies near the nucleus and in the center of the uplift generally, and that zinc is deposited around the margin.

It follows that the more recent circulation should carry more copper and iron than the earlier. In consonance with this reasoning, we find that chalcopyrite and pyrites are the latest minerals of the ore deposits, and that there is considerably more copper in the reservoir sediments in proportion to the zinc than there is in the Cambrian and Ordovician limestones, and much more than there is in the ores.

Association of the ores with jasperoid and dolomite.—The principal gangue minerals and rocks associated with the ores are calcite, dolomite, and jasperoid, the latter a siliceous rock formed by the metasomatic replacement of limestone. Calcite might easily have been derived from the wall rock of Mississippian limestone, but as that rock contains but little magnesium, that element would have to be greatly concentrated to form dolomite. The relations of the jasperoid, dolomite, and ores show that all three were derived from the same solution. The deep-well waters of the region, derived from the Cambrian and Ordovician dolomites, contain much more magnesium in proportion to the calcium than do the waters derived from the Mississippian limestones or from the Pennsylvanian shale, though they contain less silica. The deep-well waters resemble sea water, which is the most common agent of dolomitization. These waters are therefore probably the agents of dolomitization and siliceous replacement, as well as of mineralization.

Relation of ore deposits to Chattanooga shale.—Throughout the area underlain by the unbroken sheet of Chattanooga shale there are no deposits of ore, dolomite, or jasperoid. On the other hand, along the course of the Seneca fault, northeast and southwest of Seneca, Mo., there are deposits of ore, dolomite, and jasperoid as far as 8 or 10 miles within the area underlain by the shale, the solutions having ascended through the fault zone.

The Chattanooga shale caps the southwestern axial prolongation of the Ozark uplift. The water of the Cambrian-Ordovician circulation, which flows southwestward down the axis, finds itself impounded beneath this shale cap and can escape only by flowing to the lateral margins of the shale, where it can rise into the Mississippian limestone above. The area underlain by the shale north of the axis is larger than that so underlain south of the axis, and, moreover, the north edge of the shale and the outlet are at a lower elevation than the south edge; hence most of the flow and the larger territory to be leached of its metals is north of the axis. The district between the north edge of the Chattanooga shale and the inner margin of the Pennsylvanian shale is therefore favored by two circulations, the one from beneath the shale to the south and the other the direct circulation from the center of the dome. It is significant that the principal mining camps of the Joplin region are in this district.

Ore and bitumen beneath the Pennsylvanian shale.—The lead and zinc deposits at Miami, Okla., lie beneath 40 to 220 feet of Pennsylvanian shale. The ore and the wall rocks at places contain much bitumen, and the mine waters are charged with hydrogen sulphide. Ore deposits are found also in Kansas, north of Miami and several miles west of the eastern margin of the Pennsylvanian shale. Ore has been struck in drilling deep wells in Kansas many miles from the border of this shale. The mine waters charged with hydrogen sulphide are similar to the deep-well waters. The bitumen is interpreted as the residue of an oil that has lost the lighter saturated hydrocarbons by fractionation in contact with shale. The fact that this residue was left at the base of the shale indicates that the lighter hydrocarbons escaped upward. The ore solutions can not have been descending because the shale is impervious and practically no surface water penetrates the mines. The mine waters, the bitumen and the ore deposits are therefore in accord in indicating ascending currents.

Constant inflow of mine waters.—In the Miami district the deposits are overlain by a thick, practically impervious cover of Pennsylvanian shale, as noted above. The region is nearly flat, and precautions are taken to prevent surface waters from entering the shafts. The quantity of mine water is remarkably uniform and is entirely without seasonal variation, increasing only with increase of depth and extension of mining. The character of the water, as noted above, indicates its deep-seated origin, which is further shown by the regularity of supply. Without doubt there is similar deep-seated water in the other camps of the region, but its character has been masked by the larger influx of surface waters.

Geographic association of lead and zinc deposits of the eastern part of the United States with geanticlinal uplifts and marginal slopes.—In the central valley of the United States, in addition to the Ozark uplift with its four marginal mining districts, there are several areas of low, flat uplift which offer the requisite structural conditions for an artesian circulation, and the marginal slopes of all these uplifts are marked by lead and zinc deposits. In the Wisconsin uplift of the upper Mississippi Valley region the lead and zinc deposits lie around the inner margin of the Maquoketa shale. In the central part of the Cincinnati uplift, in Kentucky, there are numerous veins of galena with barite and fluorite gangue but without dolomite, and around its periphery there are small deposits of zinc ore. In the Nashville uplift, which is a southerly continuation of the Cincinnati uplift, the same general conditions prevail. Barite and fluorspar are common gangue minerals of the galena veins, but dolomite is absent.

In this report the suggestion is made that the lead and zinc ores of the Kentucky-Illinois fluorspar district have in part been derived from artesian circulating waters from the Cincinnati and Nashville uplifts, which passed beneath the Carboniferous rocks of western Tennessee and Kentucky and rose through the complicated faults of the low-lying fluorspar district. The central Kentucky well and spring waters are zinciferous, as is shown by a great number of analyses. The common occurrence of barite, the abundance of fluorspar, and the entire absence of dolomite show that these deposits are related to the veins of the Cincinnati and Nashville uplifts. On the other hand, the argentiferous character of the galena, the abundance of fluorspar, and the occurrence of igneous intrusions in the region suggest a connection between the ores and igneous activity. If this connection can be established, it would seem that there is in this region not a transition type of ore deposit but a juxtaposition of types—one type due to normal artesian circulation and the other due to igneous action.

Ore deposits of minor importance occur on the flanks of the Ouachita, Arbuckle, and Llano uplifts.

The lead and zinc deposits of eastern Tennessee and Virginia are associated with breccia zones in dolomitic limestones. The region is thrown into a series of long, parallel folds associated with thrust faults, so that artesian circulation transverse to these structures is necessarily limited. Nevertheless, Watson holds that the deposits of both Virginia and eastern Tennessee are the result of an ascending circulation of slight vertical extent, and Purdue expresses a similar view concerning the Tennessee deposits.

Scattered deposits in Pennsylvania, New York, and Canada lie for the most part in structural basins or on marginal slopes and are in such position that they seem to be the result of a local artesian circulation.

NONCORROBORATIVE EVIDENCE.

Vertical order of the sulphides.—In the ores first mined in the Joplin region, which were naturally those nearest the surface, galena largely predominated. In any soft-ground mine the ore of which reaches into the zone of oxidation galena is invariably the predominant mineral in the upper ground. In a deposit in open, cavernous ground below the zone of oxidation galena is generally in excess of sphalerite in the upper part of the ore body and sphalerite is in excess in the lower part, the iron sulphide increasing toward the bottom of the deposit. These facts led Van Hise and Bain to conclude that the present ore bodies are the results of extensive erosion and downward sulphide enrichment. The same facts led Buckley and Buehler to decide that the deposits are primarily the result of descending solutions and that the vertical order represents simply the order of solubility of the sulphides.

The conclusion reached in the present report is that galena predominates near the surface or in the upper ground because the associated sphalerite has been leached away by reason of its greater solubility, and that the increased proportion of zinc in depth is due partly to the deposition as carbonate and silicate of the zinc removed in solution from the upper part of the ore body and partly to the deposition in depth as sulphide of the zinc removed in solution from distant ore bodies. It is believed that galena is found above sphalerite in cavities because it is the habit of the two minerals to crystallize out in that relation in cavities, and that this arrangement has no connection with the order of deposition of the sulphides in descending solutions. In fact, there can be no order of sulphide deposition by descending solutions where the precipitant is present in excess, and neither Bain nor Buckley and Buehler have postulated a lack of reducing solution.

Synthesis of iron and zinc sulphides.—Dr. E. T. Allen and his associates of the Geophysical Laboratory of the Carnegie Institution have shown that pyrite and sphalerite are deposited from both acid and alkaline solutions, but that marcasite and wurtzite are deposited from acid solutions only, and they have further found that the lower the temperature the less acid is required to yield a given quantity of marcasite or wurtzite. Crystallized pyrite but no marcasite is forming in sediment from the neutral or slightly alkaline water of the springs at Sulphur Springs, Ark. The sulphides of the Joplin region are galena, sphalerite, marcasite, and pyrite. Wurtzite has been reported in small crystals from a single mine, where it is undoubtedly secondary and probably has been deposited by a descending acid solution. Since, according to the experiments, marcasite is deposited only from acid solutions and sphalerite and pyrite may be deposited from such waters, it is but natural to see reason in this for believing that the Joplin ores must have been deposited from acid solutions.

Dolomite and calcite are common gangue minerals, and the Joplin ores are so related to them as to show that they were deposited from the same solution. The association of marcasite with calcite, dolomite, and limestone is so well known that Allen was obliged to conclude that marcasite may be precipitated from solutions no more acid than calcium bicarbonate solutions. The artesian circulation was of this general character, perhaps at times slightly alkaline or slightly acid, but did not vary far either way from neutral. The ore solutions were, therefore, not strongly acid.

QUANTITATIVE TESTS OF THE ARTESIAN THEORY—CIRCULATION.

Sufficiency of the source.—The total zinc content of ores in the Ozark region mined to the end of 1912 is approximately 3,250,000 tons. For the purpose at hand we may allow as much more for future mining. As the losses in mining and milling in the Joplin district are about 50 per cent, this would give 13,000,000 tons as the original zinc content of ores mined and to be mined. We may allow twice as much more for the zinc in deposits which are too lean to work or which may never be discovered, making a total of 39,000,000 tons of zinc that has probably been leached from the Cambrian and Ordovician limestones. By figuring the volume of the Cambrian and Ordovician dolomitic limestones that might yield their metals to the artesian circulation and multiplying by the average metal content shown by Robertson's large-quantity analyses we find that the possible supply is more than a thousand times the total given above.

Sufficiency of time for the ore segregation.—Using as factors the volume and porosity of the Cambrian and Ordovician dolomites and the average zinc content of the circulation as determined from analyses of deep-well waters from Pittsburg, Kans., and Claremore, Okla., we get a zinc content of 3,000,000 tons in the water contained in the pores and interstices of the Cambrian and Ordovician rocks of the dome inside the Pennsylvanian border. To transport 39,000,000 tons of zinc the pore water would require to be changed 13 times. The average radial path pursued down the dome is about 60 miles, so that the total distance traveled would be 780 miles. By Slichter's formula we may calculate the rate of flow down the dome through the St. Peter sandstone as about 6.8 feet per year. Taking 5 feet as a fair rate and allowing for the expansion of the artesian area by erosion of the shale, we find that the time required to change the pore water 13 times would be 1,600,000 years, which is apparently not in excess of the time actually available.

Dilution of connate water.—If salt water be diluted to twice its volume 13 times in succession the solution will have only $\frac{1}{8192}$ of its original strength. When the Cambrian and Ordovician rocks were laid down in the sea the pore spaces were filled with sea water. If, as seems true, these rocks were never exposed to general subaerial erosion until the elevation of the Ozark uplift and the removal of the Pennsylvanian and Mississippian formations, then the 13 changes of pore water should start with a solution having about the constitution of ocean water. If we divide the mineral content of ocean water as found by Dittmar by 8,192, and compare the result with the average mineral content of 13 deep-well waters in the Joplin area, we find that the well waters have 9 times enough of the alkali metals, 290 times enough of the alkaline-earth metals, 3 times enough of chlorine, and 44 times enough of sulphate. The diluting waters naturally add alkaline earths and sulphate, and possibly a little of the alkali metals and chlorine, but the fact that the alkali metals and the chlorine agree so well with the calculated dilution of $\frac{1}{8192}$ seems to indicate that the calculated dilution of the connate pore water was about of the order indicated.

ENRICHMENT.

Though difference of opinion exists as to the extent of sulphide enrichment, there is no question that residual enrichment and oxide enrichment have contributed greatly to the value of many of the ore bodies of the district. In residual concentration the ore body is enriched by the solution and removal of the more soluble constituents, whether metals or gangue. Galena, owing to its greater resistance to weathering and solution, has been more generally so enriched, but for the same reason the oxidized ores cerusite, smithsonite, and calamine have also been enriched by this method, which doubtless was an important agency in the formation of the rich shallow deposits that were worked in the early days of mining.

Owing to the prevailing geologic conditions of transportation and deposition of the metals in the district, it is exceedingly difficult to distinguish in general between primary and secondary deposits. Nevertheless undoubtedly secondary sulphides have been recognized in the district. These are greenockite films upon ore minerals and gangue below the water level, galena and covellite films upon and penetrating sphalerite along cleavage planes, and stalactitic sphalerite with intergrown galena, surmounted by small wurtzite crystals. As a whole the recognizable secondary enrichment is inconsiderable.

ORIGIN OF THE ZINC AND LEAD DEPOSITS OF THE JOPLIN REGION, MISSOURI, KANSAS, AND OKLAHOMA.

By C. E. SIEBENTHAL.

INTRODUCTION.

FIELD WORK.

The writer spent the field season of 1902–3 as assistant to W. S. T. Smith in a geologic survey of the Joplin district, concerning himself chiefly with the stratigraphy and the structure. The results of that survey were published in the United States Geological Survey's Joplin district geologic folio (No. 148). During the field season of 1906–7 he was employed in a geologic survey of the Wyandotte quadrangle, adjoining on the southwest the area covered by the Joplin district and lying partly in Missouri but mostly in Oklahoma. A short season in 1910 was spent in a further investigation of the ore deposits of the Wyandotte quadrangle and in a study of some of the deeper deposits at Joplin. Another short season, in 1913, was spent on the ore deposits of the Wyandotte quadrangle, particularly in studying the recent developments at Miami.

ACKNOWLEDGMENTS.

It is not easy to give credit in exact measure to each source of assistance where everything known to the writer as bearing on the subject has been laid under contribution. It is believed that the responsibility for the various parts of the Joplin folio is made clear therein. The ideas of artesian circulation set forth in that report are reiterated in this paper. The writer regards as original to this paper, first, the recognition of the limits of the Chattanooga shale and the consequence thereof upon the artesian circulation; second, the theoretical linking together, as deposited by artesian circulating waters, of the lead and zinc deposits with the iron deposits of the central uplift region; and third, the discovery of the general occurrence of lead and zinc in the artesian waters of the bordering Pennsylvanian rocks and the sediments deposited from those waters. He hopes that something has been added to the knowledge of the chemistry of lead and zinc solutions by the experimental work herein recorded, and that the large collection of analyses of zinc-bearing waters, together with their characterization and discussion, will be useful.

In the chemical part of the paper the author has received much help which it is a pleasure to acknowledge. Prof. W. George Waring, of Webb City, Mo., made several analyses of waters and a number of analyses of reservoir sediments especially for this paper and furnished copies of many other analyses of waters and ores of the district, made in the course of his professional work. Prof. A. M. Peter, of the Kentucky Agricultural Experiment Station, contributed the section of this bulletin entitled "Zinc in Kentucky waters," and his work has been further used in the tables of analyses. Prof. W. P. Headden, of the Colorado Agricultural College, furnished several analyses, some unpublished, of zinc-bearing waters of Colorado. Prof. E. H. S. Bailey furnished notes on the artesian water at Pittsburg, Kans. Prof. H. A. Buehler, State geologist of Missouri, kindly furnished the laboratory results of four analyses appearing in a chapter by the late Dr. E. R. Buckley in "Types of ore deposits." Mr. George L. Heath, chemist of the Calumet & Hecla Smelting Works, furnished analyses of underground waters in the deep copper mines of Michigan. Dr. H. E. Merwin, of the Geophysical Laboratory of the Carnegie Institution, furnished the note on the microscopic study of the sediments of the springs at Sulphur Springs, Ark., which is incorporated in this bulletin, and together with Dr. E. T. Allen, of the same institution, has conferred with the writer regarding the precipitation of the sulphides of the metals.

Mr. Chase Palmer and Mr. Herman Stabler, of the United States Geological Survey, as responsible authors of the scheme of interpretation of water analyses herein adopted, have been freely consulted, and in particular Mr. Palmer has been a constant source of help in the study of the chemistry of the ore solutions. Mr. Roger C. Wells, of the United States Geological Survey, made the experimental studies of the solubility of sphalerite in the presence of calcite appearing herein and has given generously of his time to helpful discussion of the problems touching the side of physical chemistry. Mr. E. C. Sullivan, while connected with the United States Geological Survey, made the determinations of the relative solubilities of the bicarbonates of lead and zinc as compared with the carbonates of those metals.

The laborious and tedious task of recalculating the large number of water analyses to the geochemical form has been conscientiously performed by Mrs. Marion L. Clark.

Among those who furnished analyses, samples of water, or samples of sediment are Messrs. J. N. Wells and Benjamin Cuthbertson, superintendents of the Pittsburg Water Supply Co., Pittsburg, Kans.; J. P. Gooch, superintendent of waterworks at Vinita, Okla.; W. T.

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Whitaker, of Pryor Creek, Okla.; F. H. Hawkins, superintendent of waterworks at Columbus, Kans.; J. T. Marsh, manager of the Clinton Light & Power Co., Clinton, Mo.; W. E. Blackwell, chief engineer of Afton waterworks, Afton, Okla.; L. C. Church, Miami, Okla.; Charles Strong, chief engineer at State Hospital No. 1, Fulton, Mo.; D. K. Greger, Fulton, Mo.; W. J. Warner, manager of the Belcher Water Bath & Hotel Co., St. Louis, Mo.; W. O. Buck, superintendent of United States Fish Hatchery, Neosho, Mo.; C. E. Wells, Sulphur Springs, Ark.; R. D. Silver, St. Charles, Mo.; C. J. Light, Lanagan, Mo.; and others.

THE OZARK UPLIFT.

GEOGRAPHY.

The Ozark uplift is a low asymmetric dome with rudely elliptical outline, lying in southern Missouri, northern Arkansas, southeastern Kansas, and northeastern Oklahoma. It is roughly bounded on the north and northeast by Missouri and Mississippi rivers, on the west by Spring and Neosho (Grand) rivers, on the west and south by Arkansas River, and on the southeast by Black River and some of its tributaries. To the north and west it merges into the Prairie Plains; to the east and southeast it passes into the low-lying Gulf Coastal Plain; on the south it is separated from the Ouachita Mountains by the valley of Arkansas River. The uplift as a whole is a table-land bounded by long, low northern and western slopes whose inclination is generally imperceptible to the eye, and for much of its extent by an abrupt southern slope facing the open valley of Arkansas River. Near and parallel to its southern margin the uplift culminates topographically in the Boston Mountains, a long, narrow plateau rising to an elevation of 2,000 feet. The plains that surround the uplift have a general altitude of 500 to 750 feet. The central portion of the Ozarks is an upland lying somewhat below the crest of the Boston Mountains. These features are well shown in the accompanying generalized topographic sketch map (Pl. I).

The erosional forms throughout most of this area are those characteristic of an early mature topography in a region of nearly flat-bedded rocks of varying degrees of hardness, the dip of which differs but slightly from the general surface slope. The entire northern slope of the uplift consists of a succession of broad plateaus. Over much of the region, especially the northern and western slopes, these broad uplands are cut by moderately shallow, open valleys, whose depth does not exceed a few hundred feet. Toward the south and east the dissection is greater, the forms are more rugged, and the plateau character is somewhat less evident, especially near the east end of the Boston Mountains. The drainage of the uplift is radial, many streams flowing outward to the marginal rivers. Of these streams Spring River is the largest in the Joplin region.

AREAL GEOLOGY.

Pre-Cambrian rocks.—Van Hise and Leith[1] describe the pre-Cambrian rocks of southeastern Missouri as pre-Cambrian islands surrounded by Cambrian sediments. The pre-Cambrian system consists mainly of granites, felsites, porphyries, and porphyritic breccias. At Pilot Knob and in the adjacent area are found water-deposited rocks which comprise porphyry conglomerates, fine-grained beds of the same character, and well-bedded iron ores and ferruginous slates. The porphyry sediments and the iron-bearing rocks are interbedded in such a way as to suggest a deposition under water of nonfragmental iron-formation material similar to that in the Lake Superior region, this deposition being interrupted by the accumulation of volcanic material which itself was to a considerable extent worked over by water. The iron ores found at Iron Mountain occur largely as great irregular masses and veins in the porphyry and may be of different origin. The relations of the pre-Cambrian sedimentary rocks to the massive granites and porphyries are not known. The unaltered horizontal Paleozoic rocks rest on the deeply eroded crystalline rocks, the conglomerates adjacent to Pilot Knob and Iron Mountain containing numerous bowlders of iron ore.

Cambrian and Ordovician rocks.—The oldest Cambrian formation in southeastern Missouri is the Lamotte sandstone, which is the basal formation overlying the crystalline rocks in the disseminated lead district. The lower part of the formation is conglomeratic, containing pebbles and bowlders of the pre-Cambrian crystallines. The Lamotte sandstone occupies the depressions in the higher portions of the pre-Cambrian nucleus and also in the basins dipping away from it. This sandstone in depth holds water under strong artesian pressure, so that in drilling in the mines care is taken to avoid penetrating it, and when it is penetrated the holes are plugged to prevent the artesian flow from rising into the mines. Overlying the Lamotte sandstone is the dolomitic Bonneterre limestone, in the lower part of which the disseminated lead ores are chiefly found. In the shaly beds of transition from the Lamotte sandstone below to the Bonneterre limestone lead ore is also found; but here the galena is usually more or less mixed with the sulphides of iron, copper, nickel, and cobalt.

Above the Bonneterre limestone there are several other formations of dolomitic limestone, shale, and sandstone, among others the Potosi, Gasconade, Roubidoux, Jefferson City, St. Peter, Joachim, and Kimmswick formations, all belonging to the Cambrian and Ordovician systems. The St. Peter sandstone, of Ordovician age, is the

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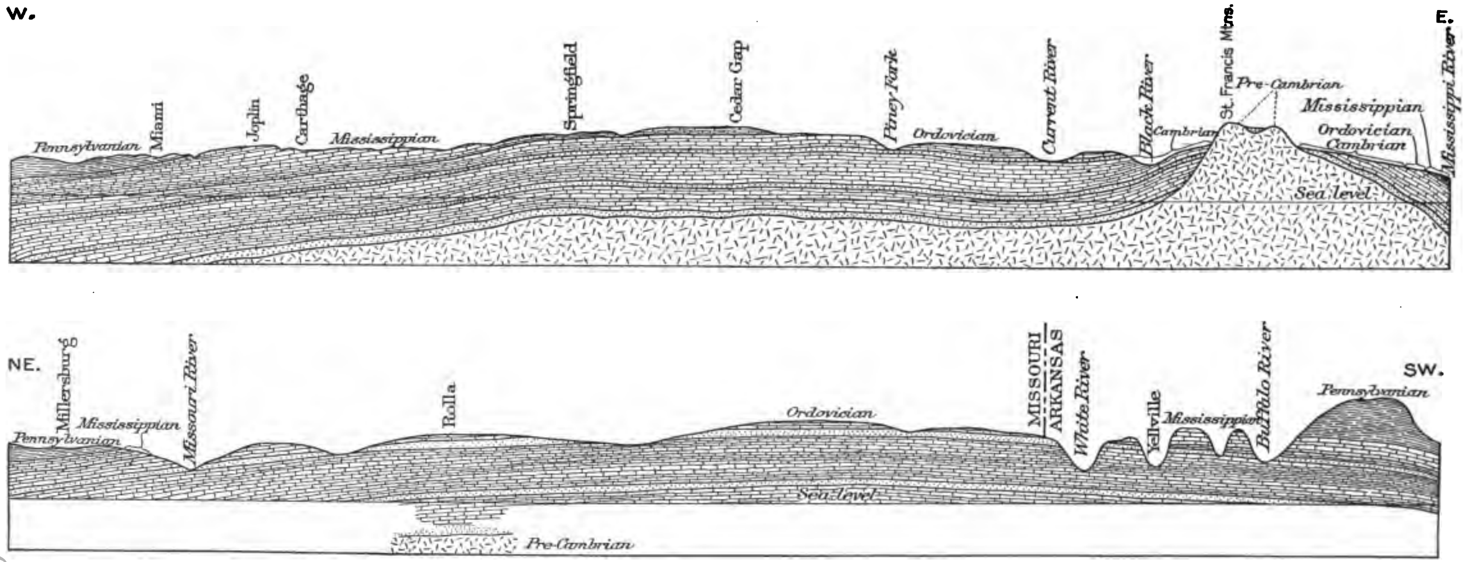
[1] Van Hise, C. R., and Leith, C. K., Pre-Cambrian geology of North America: U. S. Geol. Survey Bull. 360, pp. 740-741, 1909.



GEOLOGIC CROSS SECTIONS OF THE OZARK UPLIFT.

After Buckley.

uppermost of the three "Saccharoidal" sandstones of Swallow, which are shown in the structure sections (Pl. II).

Silurian rocks.—Formations of Silurian age are found on the southern and northeastern borders of the uplift, but they are wanting in all the western part of the Ozark region and hence need not be here considered.

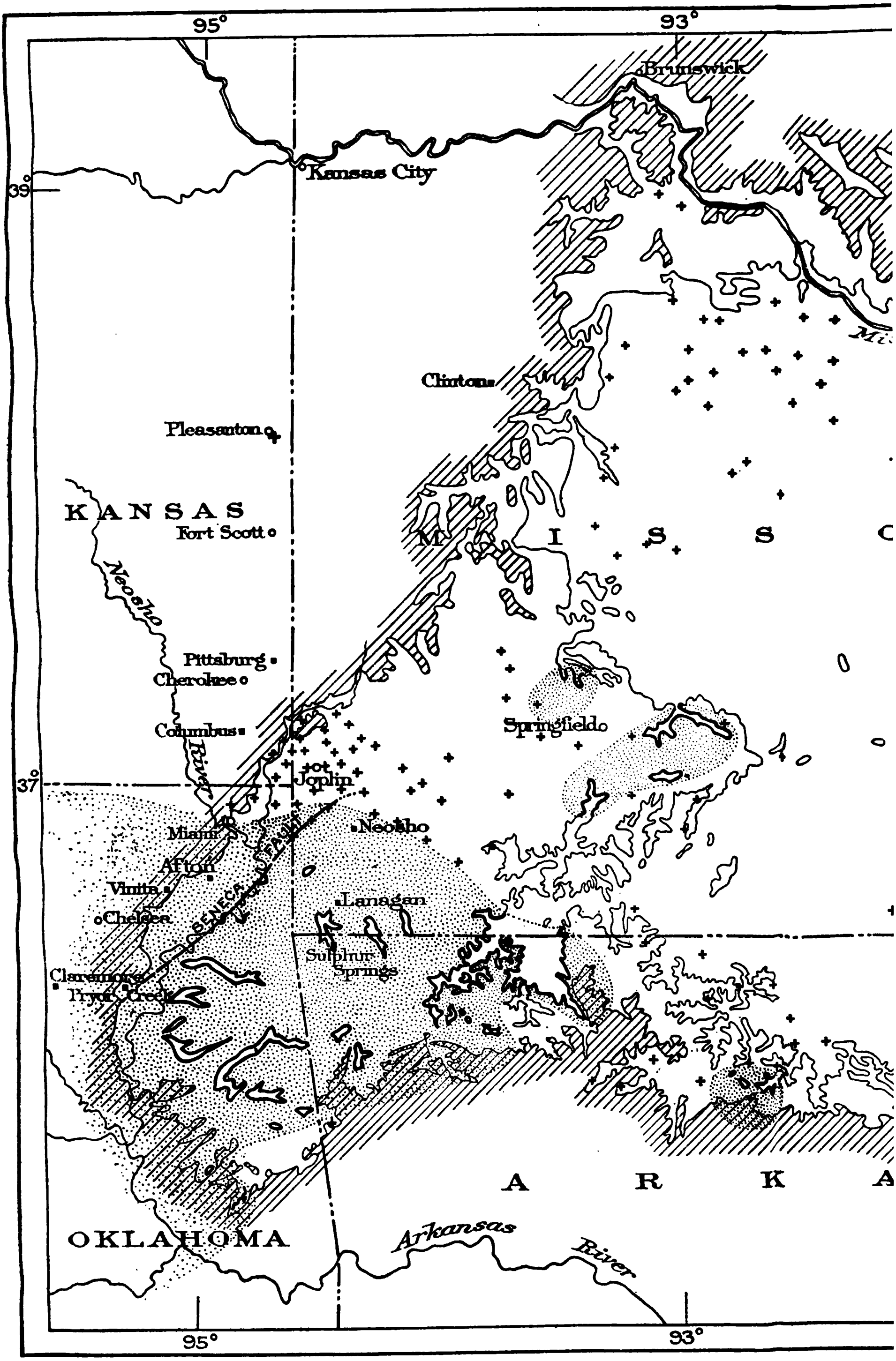
Devonian rocks.—Limestones of Devonian age are found along the northeast quarter of the border of the uplift. On the southern border of the uplift there are interrupted outcrops of the phosphate-bearing Sylamore sandstone member of the Chattanooga shale. The chief Devonian formation of interest in connection with the ore deposits of the Joplin region is the Chattanooga shale. This formation underlies the Mississippian rocks and forms an apparently continuous sheet throughout that part of the uplift southwest of a line drawn through Granby and Cassville, Mo., and Eureka Springs, Ark., as shown by the stippled area on the map (Pl. III), on which the heavy black line represents the outcrop of the shale and the light line represents its horizon where it is absent. The stippled area shows where the shale is present, though covered by other formations; in other words, where it is capable of preventing the ascent of the Cambrian-Ordovician circulation into the Mississippian rocks. In this area wherever the drainage has cut deep enough to expose the horizon of the Chattanooga shale, that formation has always been found. Although the border of the underlying shale body may not be as smooth as indicated on the map, nevertheless that line must closely approximate the margin of the formation. The shale was struck in deep wells at Centralia, Welch, and Peoria in Oklahoma, and at Seneca, Neosho, Granby, and Exeter in Missouri. It is absent at Miami and Quapaw, Okla., at Joplin, Carthage, Wentworth, McDowell, Aurora, and Springfield, Mo., and in some drill holes at Granby, Mo., indicating that the latter place is just on the border of the shale. The presence or absence of the shale at the places just mentioned fixes rather closely the location of the margin of the formation. In the vicinity of Eureka Springs, Ark., the tributaries of White River have cut below the horizon of the shale, so that its exact limits can be determined. From this region the southern limit of the formation seems to bear southwest by Fayetteville, Ark., to the Oklahoma line, near the village of Morrow. Farther southwest, from this point to Arkansas River, the limit of the shale is determinable from several exposures of its horizon along the valley of Sallisaw Creek. In this area underlain by the Chattanooga, the shale reaches its maximum thickness—more than 90 feet—on Neosho (Grand) River, at the mouth of Honey Creek and near Spavinaw village, from which locality it thins away in all directions, northward to 5 feet at Seneca, westward to 40 feet at Claremore, southward to 20 feet at Marble, and eastward to 60 feet at Noel, and to 12 feet north of Eureka Springs.

Outcrops of the Chattanooga shale are mapped on Sac River north of Springfield, Mo., and it is reported to have a thickness of 7 feet in the Pennsylvania shaft near Ash Grove, indicating an area of the shale in that vicinity. Another area of the Chattanooga, southeast of Springfield, is mapped from outcrops on the tributaries of James Fork. A third small area is mapped from exposures in the vicinity of St. Joe, Ark.

It is evident from the attenuated margin of the shale and its discontinuous outcrop that it either never extended much farther up on the Ozark dome or that, if it once did so extend, it has since been removed by erosion. In either event it was not present to separate the Cambrian-Ordovician and Mississippian underground circulations over the larger part of the uplift.

Mississippian rocks.—The Mississippian series, more particularly the lower part of it, comprising the rocks of Osage and Kinderhook age and excluding the shales and sandstones (Chester group) of the upper portion, varies from 200 to 350 feet in thickness. The thickness in detail is: In Arkansas, at Batesville 250 feet, at Yellville 325 feet, at Fayetteville 325 feet; in Oklahoma, at Tahlequah 300 feet, at Fairland 340 feet; and in Missouri, at Joplin 350 feet, at Springfield 300 feet, at Sedalia 200 feet, in Moniteau County 190 feet, at St. Louis 670 feet. These thicknesses, regularly disposed about the margin of the uplift, indicate a much greater former extension of the Mississippian upon the dome, and in fact Nason reports lower Carboniferous (Mississippian) fossils in limestone in a collapsed cave within 20 miles of the crystalline nucleus of the uplift. It is probable, however, that this inner extension of the Mississippian was considerably attenuated.

In the Joplin region the whole vertical section from the base of the Chester rocks to the underlying Chattanooga shale is included in the Boone formation. About 100 feet below the top of the Boone there is a stratum of oolite, from 2 to 8 feet thick, which has been named the Short Creek oolite member. This oolitic limestone occurs throughout the Joplin district quadrangle and the eastern half of the Wyandotte quadrangle and has been found also at Granby, Aurora, and Springfield, Mo., and near Harrison, Ark. Although, perhaps, not persistent throughout this entire area, it is nevertheless a useful stratigraphic datum plane. That part of the Boone above the oolite consists of limestone and light-colored chert interbedded. At some places, as at Carthage, the limestone not far above the oolite is massively bedded and the chert is very subordinate in amount and is confined to the partings between the limestone beds. The Carthage



GEOLOGIC MAP OF THE OZARK UPLIFT SHOWING MINING CAMP

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quarries are at such a place. A hundred feet below the Short Creek oolite the Grand Falls chert member comes in, with a thickness of 25 to 40 feet or so. At this horizon the Boone generally contains a great deal of light to dark blue chert, interstratified with drab to bluish fine-grained limestone. At Grand Falls, on Shoal Creek just south of Joplin, the original chert constituted perhaps two-thirds of the total mass and the remaining third was limestone, which has been replaced for the most part by jasperoid. This replacement has converted the cherty beds into a massive resistant ledge known as the Grand Falls chert member, and in these rocks are found the deposits of sheet ground ore in the vicinity of Joplin, Carl Junction, and in the area from Oronogo to Duenweg. The Grand Falls chert is reported to occur at places in the bluffs of Shoal Creek as far southeast as Granby. Between the Short Creek oolite and the Grand Falls chert the rocks consist of interstratified chert and limestone similar to the chert and limestone above the oolite, and in this, as in that series, there is usually a development of massively bedded limestone with little chert which here is not far below the oolite. In places on the outcrop these heavy beds of limestone seem to merge into one massive ledge without apparent parting. Such ledges have been quarried at the Joplin limekiln quarry and test openings have been made in others west of Grand Falls and northwest of Galena. Below the Grand Falls chert there is a series of limestones and lighter cherts, which weather chalky and are very irregularly bedded at places, especially where exposed in the southern part of the Wyandotte quadrangle. Toward the north the limestone of this series becomes shaly in part, forming the bluish shale or shaly limestone which is struck in the deep wells about Joplin and which was described from the Mystic shaft southwest of Joplin.[1] Farther east this characteristic becomes still more pronounced, until, in the vicinity of Aurora, just above the base of the series, there is a considerable thickness of fine-grained bluish shale, in places breaking into massive slabs, which stain yellow. This shaly portion is locally ore bearing and has been mined at Springfield, McDowell, Aurora, Stotts City, southwest of Joplin, and at Hornet, Mo., and near Galena, Kans. At the base of the formation, just above the Chattanooga shale, there has been distinguished in the Wyandotte quadrangle and to the south and east the St. Joe limestone member, from 12 to 30 feet or more in thickness, consisting of massive limestone, which is practically without chert and which usually forms a projecting ledge, owing to the erosion of the shale beneath.

The formations of the Chester group are well developed along the southern margin of the uplift and extend northward along the western margin to the southern line of Kansas. In the vicinity of Joplin the Chester rocks, corresponding approximately to the Batesville and Fayetteville formations, occur in sink-hole depressions. These rocks have been described in the Joplin folio as the Carterville formation. Such outcrops are known also at Granby and Aurora. In the Wyandotte quadrangle the Boone is overlain, slightly unconformably, by 20 to 40 feet of crystalline flaggy limestone, which is in places heavy bedded and massive, is in part oolitic, and is free from chert. This limestone grows arenaceous toward the top and is succeeded by a calcareous sandstone that on the weathered outcrop is a characteristic sandstone containing fossils which show that it is to be correlated with the Batesville sandstone. At Miami, Okla., the ore deposits first worked were found in this sandstone where it had been let down upon the Boone owing to the solution and removal of the underlying limestone, the bed between the sandstone and the Boone. Overlying the sandstone there is a black fissile unfossiliferous shale which in places, especially toward the north, gives way to a soft, drab clay shale, crowded with the characteristic fossils of the Fayetteville formation. Overlying the shales are limestones which also contain Fayetteville fossils and are generally in part oolitic. The formation is nearly everywhere topped with reddish sandstones, presumably equivalent to the Wedington sandstone member of the Fayetteville formation, described in the Fayetteville folio.[1]

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[1] **Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 2, 1907, reprinted 1914.**

Pennsylvanian rocks.—The formations of the Pennsylvanian series of the Carboniferous follow the Chester rocks conformably along the southern border of the uplift. On the western border, however, there was a warping and tilting of the western part of the uplift by which the southern portion was elevated and the northern portion depressed and which caused the Pennsylvanian to transgress far upon the dome, as already described by the writer.[2] The transgressing formation, the Cherokee shale, in Oklahoma, Kansas, and Missouri, is thus younger in age than the Pennsylvanian formations bordering the uplift on the southern and southwestern margins. When the transgressed limestone area was land, before the deposition of the Cherokee, it was subjected to erosion and solution with the result that a karst topography was developed over most of the area. Upon this karst surface the shale was laid down, filling up the sink holes and closed valleys and spreading far over upon the dome, its contact with the underlying Mississippian rocks being what the writer[3] has elsewhere called a solution unconformity, marked by a basal breccia instead of a basal conglomerate. Afterward, when the main body of shale was carried away by erosion, which extended down to the level of the limestone, the shale in the sink holes and depressions remained as "roots" of the former deposits, and these constitute the sink-hole shale patches which dot the upland part of the dome, and many of which contain thick beds of coal. Patches of shale have been reported in Crawford, Phelps, and Dent counties within a few miles of the crystalline nucleus of the Ozark area, and the sediments laid down in the Pennsylvanian sea undoubtedly covered the dome with deposits of shale and sandstone well up to the pre-Cambrian center. It is in the "basal breccias" at the contact of the shale and the limestone that the "open-ground" or "confused-ground" deposits of lead and zinc ore are found in the Joplin region.

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[1] Adams, G. I., and Ulrich, E. O., U. S. Geol. Survey Geol. Atlas, Fayetteville folio (No. 119), 1905.

[2] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, pp. 190-192, 196, 211-213, 1908.

[3] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), pp. 8, 9, 1907.

The Pennsylvanian rocks are chiefly shales, though they include interbedded sandstones and limestones, and this statement is true of the older Pennsylvanian formations, which outcrop along the Arkansas border of the uplift as well as of the Cherokee shale, which outcrops on its west and north sides. The essentially shaly character of these formations is here emphasized, as it is indispensable to the contention that the Pennsylvanian rocks form an effective cover for the artesian water circulating through the dome.

Post-Carboniferous rocks.—The Tertiary and Quaternary rocks of the Mississippi Embayment overlap the uplift on its southeastern border. Earlier gravels are found on the uplands over most of the dome and later gravels are found on terraces in the valleys of the larger streams, but these formations are of interest principally for their record of the physiographic history of the region in post-Carboniferous time, so that it will not be necessary to describe them at this place.

STRUCTURAL GEOLOGY.

The Ozark uplift is a broad geanticline in which the strata have local dips though their general inclination is imperceptible except at the southern margin, along the south side of the Boston Mountains, where the level-bedded strata that make up these mountains break off into a southward-dipping monocline. The broad essential structure of the uplift is shown in the two horizontal cross sections forming Plate II, which is modified from diagrams prepared by Buckley.[1] These sections show plainly that the uplift reaches its structural culmination near the center of the area bounded by the outcropping Pennsylvanian shales. The north-south arching of the uplift is also shown by the relations of the outcrops of the Cambrian and the Ordovician rocks to the topography—in the way these outcrops in the valleys of the southward flowing streams rise up as they approach the center of the uplift.

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[1] Buckley, E. R., Lead and zinc deposits of the Ozark region: Types of ore deposits, p. 129, 1911.

Superimposed upon the geanticline are faults, folds, and quaquaversal domes. The region of the St. Francis Mountains, the crystalline nucleus of the uplift, has, in some sort, a quaquaversal structure. The Cambrian rocks, which surround the crystalline rocks, dip away from them on all sides and display a synclinal structure between the crystalline areas. A small area in Crawford County [1] is described as composed of rocks showing quaquaversal structure. A small area in Camden County known as the Decaturville dome [2] has a nucleus of pegmatitic granite, about which the Cambrian and Ordovician rocks dip away on all sides. Other quaquaversal structures upon the Ozark dome are shown on the map forming Plate IV. This map has been greatly generalized, partly for simplicity but mainly owing to the absence of detailed mapping over much of the area. It is offered as a preliminary map only, showing the structure of the southwestern half of the uplift, but it is believed to present a fairly true picture of the main structural features of that part of the Ozark region. The structural contours are based upon the upper surface of the Chattanooga shale, or where that is lacking upon the contact of the Mississippian with the lower rocks. It is thus the result of an attempt to reproduce the present contour of the surface on which the Carboniferous rocks were laid down. The culmination of the uplift as shown is in or about Wright County, but the map shows also another interesting area almost as pronounced, This upraised area appears to be the culmination of an anticlinal fold extending northwestward to Joplin from a point 50 miles southeast of Berryville. In the Joplin district geologic folio the writer has described the plunging north end of this fold as the Joplin anticline. As a result of the existence of this upraised area near Berryville, the axis of the southwestern prolongation of the uplift is shifted much farther southward than a study of the areal geology would indicate. From the culmination of the uplift in Wright County the axis extends southwestward to the Berryville area and then swings nearly due west to the western border of the uplift. The relation of this southerly location of the axis to the ore deposits of the Joplin district is discussed on page 199.

The folds and faults in northern Arkansas have been discussed by Hopkins [3] and Branner.[4] Their trend is in the main north of west, paralleling rather closely the north face of the Boston Mountains.

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[1] Hughes, V. H., Reconnaissance work: Missouri Bur. Geology and Mines Biennial Rept. of State geologist to Forty-sixth General Assembly, pp. 48-54, 1911.

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 432-434, 1894. Shepard, E. M., Spring system of the Decaturville dome, Camden County, Mo.: U. S. Geol. Survey Water-Supply Paper 110, pp. 113-125, 1905.

[3] Hopkins, T. C., Marbles and other limestones: Arkansas Geol. Survey Ann. Rept. 1890, vol. 4, pp. 401-417, 1893.

[4] Branner, J. C., The zinc and lead region of north Arkansas: Arkansas Geol. Survey Ann. Rept. 1892, vol. 5, pp. 36-63, 1900.

Toward the west, the Walnut Ridge fold and fault bears northwestward and comes into general alignment with the folds and faults of Greene County, which have been described in some detail by Shepard.[1] In the Joplin district folio the present writer has described the Joplin anticline, which passes through Joplin with a northwesterly trend. In another publication[2] he has described the Horse Creek anticline, which extends from a point south of Vinita, Okla., in a direction north of east for about 30 miles, and also the Seneca fault, in the same region, in general double, letting down a block 200 to 1,500 feet wide and more than 70 miles long, with a maximum displacement of 125 feet. Doubtless there are numerous folds and faults throughout the central region of the uplift, but that territory has been explored only by rapid reconnaissance surveys and not much of the detail of its structure is known. Farther east, in Washington and St. Francois counties, there are faults of very considerable throw and extent, which have been mapped and described by Buckley.[3]

HISTORICAL GEOLOGY.

In Cambrian and Ordovician time the crystalline rocks of the St. Francis Mountains formed a rugged archipelago and their erosion furnished in part the material making up the "First," "Second," and "Third" sandstones of Swallow, which, with the associated limestones, were spread out over Missouri and the adjacent States east, south, and west. At the close of Cambrian and Ordovician sedimentation the Ozark area was lifted slightly above the water level and deposition ceased over most of the area. Silurian deposits on the southern and northeastern borders of the uplift indicate that the land area at that time corresponded in those directions with the borders of the present uplift. The absence of Silurian rocks on the north and west at the Devonian contact points to an extension of the Silurian land in those directions. In the succeeding period, however, the Devonian sea covered the western half of the uplift and Devonian black shale (Chattanooga shale) was laid down over northwestern Arkansas and the southern part of southwestern Missouri, and Devonian limestone was laid down on the north and east. This period of sedimentation was apparently succeeded by a period of slight elevation during which the Chattanooga shale was partly eroded, leaving several isolated areas separated from the main area in southwestern Missouri, northwestern Arkansas, and northeastern Oklahoma. With the beginning of the Mississippian epoch the land subsided and the limestones of that time were laid down over most if not all the Ozark area.

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[1] Shepard, E. M., A report on Greene County: Missouri Geol. Survey, vol. 12, pp. 155-160, 1898.

[2] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, pp. 197-198, 1908.

[3] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, vol. 9, pp. 80-84 [1909].

The Mississippian deposition was closed by an elevation which raised considerably above water most of the Ozark area except that portion south and west of a line drawn from Miami, Okla., to the vicinity of Fayetteville, Ark. The limestone upland was then subjected to erosion and solution, and upon it was developed a typical karst topography, with sink holes, closed valleys, and underground passages. The southern border of the uplift was then depressed and pre-Cherokee Pennsylvanian formations were laid down. An oscillating warp next skewed the western part of the uplift, making land out of the region which is now the Boston Mountains and depressing the northwestern and northern margins of the uplift so that the Cherokee shale transgressed far upon the Mississippian rocks in those areas, and in fact practically if not quite completely covered that part of the uplift lying north of the Boston Mountains. The superficial depressions in the limestone were filled and many of the subterranean openings were wholly or partly filled by shaly sediments which, together with the residual chert and limestone, formed the basal breccia that was afterward mineralized.

About the close of Alleghany time, or the middle of the "Lower Coal Measures," an uplift raised the Ozark region above water. At the close of the Carboniferous period the region shared in the general deformation, which gave it much the same contour that it now has. After the close of the Carboniferous period the region was for a long time subjected to subaerial erosion, which eventually reduced it to a peneplain. During this time chert nodules were etched from their limestone matrix, reduced to smaller size, and rounded by water. In the later part of the period, when the land stood near base-level, the gravels must have covered much of the surface with a heavy mantle and lain deeply in the wide, shallow waterways and drainage basins. The deposition of the lignitic Eocene of southeastern Missouri was followed more or less closely by the uplift of the Ozark region to nearly its present position—an uplift that quickened the sluggish streams of the peneplain, which swept the accumulated gravels down the sides of the dome and out upon the Mississippi delta plain. The rejuvenated streams attacked the peneplain with renewed energy, cutting canyons 250 to 300 feet or more in depth and removing the Cherokee mantle from most of the area. A slight subsidence, which resulted in the deposition of sand and gravel terraces in the canyon bottoms, was followed by an elevation which removed most of the terrace material from the valleys.

UNDERGROUND CIRCULATION IN THE OZARK REGION.

IMPORTANCE OF THEORIES OF CIRCULATION.

In any discussion of the origin of the lead and zinc ores of the Ozark region the form of the conception of the circulation of the underground waters must play an important part and must be especially considered in any discussion of the deposition of these ores in southwestern Missouri. An attempt will be made under this general heading to present a conception of this circulation in a cross section of the Ozark dome from its summit to its margin in the southwestern or Joplin district and to represent its development by stages to the present time and condition. In this attempt the principles developed by King and Slichter in their experimental work with homogeneous materials are applied to the heterogeneous strata and structures of the geologic cross section of the dome.

THE ARTESIAN CIRCULATION.

The circulation of underground water in the Ozark dome is doubtless limited principally to the stratified rocks above the pre-Cambrian basement complex. The circulation of water through the cleavage planes and joint systems of the crystalline rocks must be relatively slight. The circulation in the upper part of the stratified rocks must largely exceed that in the lower part, which, however, has the accessory factors of increased temperature and pressure, so that it may be questioned which part of the circulation is the more effective for solution and transportation.

In the preceding pages and on the geologic map (Pl. III) it has been shown that the Cambrian and Ordovician rocks make up the central and eastern parts of the dome except the small nucleal area of crystalline rocks, that the nonpersistent Chattanooga shale is limited to the southwestern part of the dome, that the shaly phase of the Kinderhook is confined to the northern half of the dome, that the Mississippian formerly extended nearly to the summit of the dome, and finally that the Pennsylvanian shale formerly covered almost all if not quite all of the dome.

When, after the close of deposition of the Pennsylvanian shale, the Ozark dome was elevated into land, the crest of the dome was subjected to erosion, which then, or as soon as the overlying Pennsylvanian shale and other rocks were removed, exposed Cambrian and Ordovician rocks. The exposed Cambrian and Ordovician sandstones and dolomitic limestones dipped away from the crest of the dome on all sides and were overlain on the flanks by the impervious shale of the Pennsylvanian, forming the receiving area of a practically perfect artesian system, a cross section of which would correspond almost exactly with Slichter's diagram[1] (reproduced here as fig. 1), showing the flow of water in a series of inclined pervious beds lying between two impervious beds.

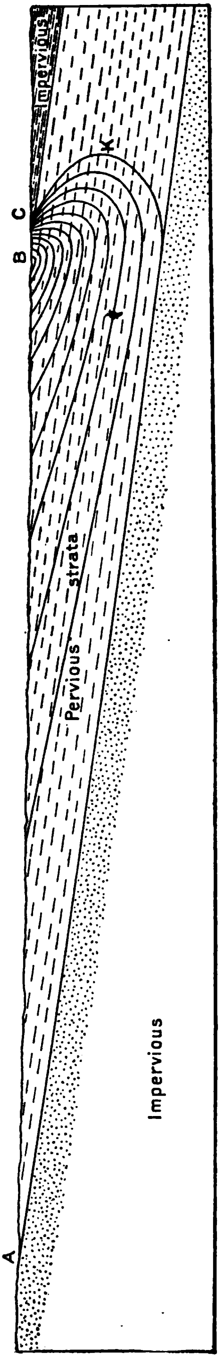

FIGURE 1.—Diagram showing artesian circulation (from Slichter). The area from A to B is a receiving area, which absorbs the rainfall; the area from B to C is an area of outflow of ground water. K is the farthest point reached by the artesian circulation beneath the impervious shale cover.

At that time the ground-water level may be assumed to have been near the surface of the crest of the dome. Water falling upon the surface would sink into the ground and would then flow outward down the slope of the dome into the partings between the strata. If the whole stratified section of the dome be taken into account, the crystalline basement furnishes the lower practically impervious limit. As the impervious Pennsylvanian shale overlaps upon the flanks of the dome and forms the upper impervious limit, the requisite conditions of the diagram are established. In the diagram the water is represented as taking a fairly direct course from K to C. This obviously is its main path—that pursued by the main volume of flow—but undoubtedly the whole triangular area between C, K, and the base of the upper impervious bed above K is filled with water moving with less velocity toward C. So we may reason that the undersurface of the upper impervious bed for some distance from its margin is the upper limit of a sheet of water flowing upward to C. This reverse flow is distinguished here because in the present writer's opinion it has an important relation to the theory of ore genesis here presented. The writer conceives that this body of stagnant or slowly moving water in the broken ground or basal breccia just below the Pennsylvanian shale was favorable to the escape of carbon dioxide and hence to the deposition of the ores.

The general outline of the circulation having been established from this diagram, it will be helpful to picture, by a series of diagrams, the stages in the development of the circulation as the Pennsylvanian shale border is eroded farther and farther down the flanks of the dome. In order that the relation of the different stages to each other may be perfectly clear the same diagrammatic radial cross section will be used in each diagram of this series, modified for each stage to represent the progressive erosion of the dome.

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[1] Slichter, C. S., The motions of underground waters: U. S. Geol. Survey Water-Supply Paper 67, p. 36, fig. 13, 1902.

At the stage represented in figure 2 the Pennsylvanian shale has been eroded to B, or perhaps has never extended beyond that point. The circulation will thus be in a very early stage of development. The ground-water level shown by the dotted line is near the surface, and the underground journey of the water from the points where it enters the circulation to the points where it emerges at the margin of the shale is not long. Theoretically, the circulation sweeps through the whole column of stratified rocks, but as a matter of fact the circulation in the lower rocks is infinitely slower than in the rocks nearer the surface. As the strata making up the slope of the Ozark dome are of different degrees of porosity and are separated by parting planes through which the water circulates more freely, they constitute an artesian slope, and water under artesian head may be found not only beneath the Pennsylvanian shale but also within the area of the slope from which that shale has been eroded.

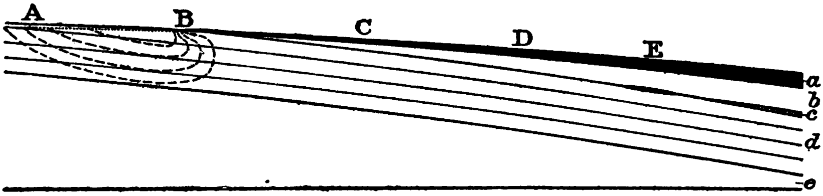


FIGURE 2.—Diagram showing early stage in Ozark artesian circulation. A–E, Stages in erosion of Pennsylvanian shale. *a*, Pennsylvanian shale; *b*, Mississippian limestone; *c*, Chattanooga (Devonian) shale; *d*, Ordovician and Cambrian rocks; *e*, pre-Cambrian rocks.

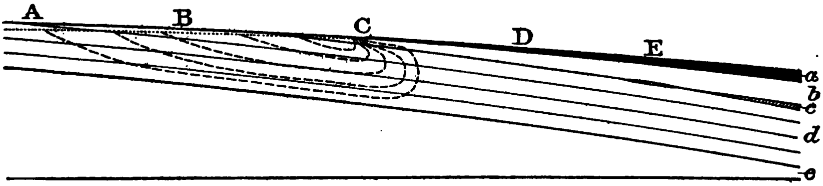


FIGURE 3.—Diagram showing later stage in Ozark artesian circulation. A–E, Stages in erosion of Pennsylvanian shale. *a*, Pennsylvanian shale; *b*, Mississippian limestone; *c*, Chattanooga (Devonian) shale; *d*, Ordovician and Cambrian rocks; *e*, pre-Cambrian rocks.

At the stage shown in figure 3 erosion has progressed until the inner margin of the Pennsylvanian shale rests at point C. The circulation is well established but is practically confined to the Cambrian and Ordovician rocks. The direction of flow at the point B, which in the preceding stage was upward, has under artesian pressure been reversed and is now directly downward to the underground water table and then outward down the slope of the dome. The flow at C is upward under hydrostatic pressure, which drives the flow on beneath the Pennsylvanian shale cover for some distance, producing a reverse flow inward beneath the shale, as explained above.

The erosion of the Pennsylvanian shale at the stage shown in figure 4 has proceeded until its inner edge rests at point D. The flow is now downward at C as well as at A and B, and is upward under strong artesian pressure in the strip of territory adjacent to the edge of the shale. The Pennsylvanian shale is probably unbroken down the sides of the dome, and the water inclosed in the sedimentaries beneath the shale is practically stagnant. The flow pursues the theoretical paths of the cross section, modified by the conditions of more active and less active flow in various parts of the stratified series. In the absence of the Chattanooga shale and of the more shaly phases of the Kinderhook, the circulation of the Cambrian and Ordovician rocks and the Mississippian rocks is one, the contact being no more capable of separating them than is the contact between two individual limestone beds in either series. Water falling on the central area of the dome out to the circle drawn through D, except the run-off and the water evaporated, is drawn into the sedimentary rocks, flows down the dip of the rocks, and rises to the surface again in the territory adjacent to the shales.

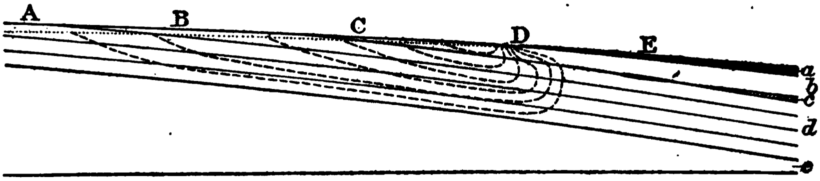
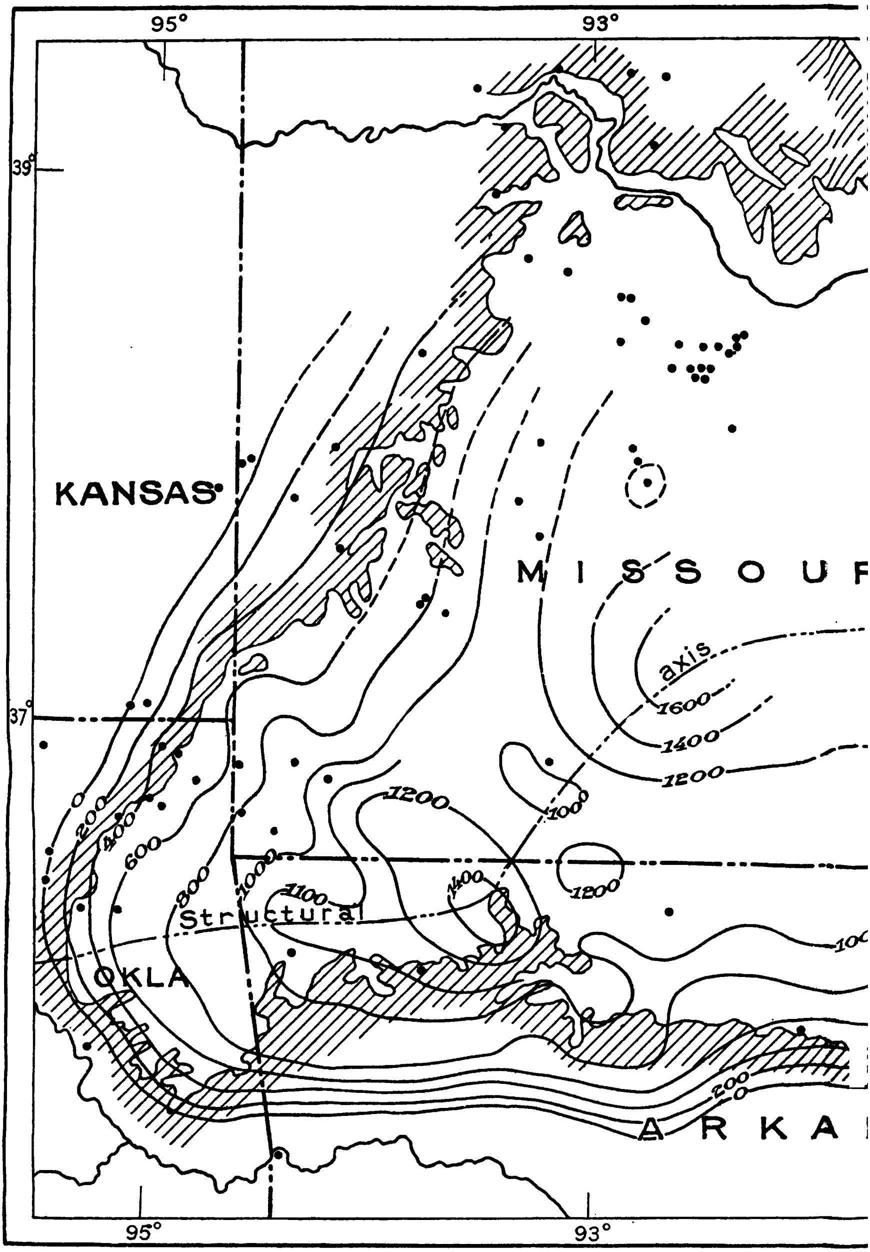


FIGURE 4.—Diagram showing still later stage in Ozark artesian circulation. A–E, Stages in erosion of Pennsylvanian shale. *a*, Pennsylvanian shale; *b*, Mississippian limestone; *c*, Chattanooga (Devonian) shale; *d*, Ordovician and Cambrian rocks; *e*, pre-Cambrian rocks.

The foregoing diagrams (figs. 2, 3, and 4) represent the orderly development of the underground circulation of the dome with progressive erosion of the overlying impervious cover, the Pennsylvanian shale, uncomplicated by the intercalation of the Chattanooga shale.

Another diagram may be added to show the complexities imposed upon the circulation by the occurrence of lenses or larger bodies of shale intercalated between the Cambrian and Ordovician limestones and the Mississippian limestones. The diversions forced upon the ascending currents by these perched water tables are similar to those imposed by the edge of the Pennsylvanian shale. Figure 5 shows also the condition that exists when the Pennsylvanian shale has been cut through farther down the dome and when strong artesian currents rise to the surface.



MAP SHOWING DEFORMATION OF SOUTHWESTERN HALF OF THE OZA
WELLS.

Figures on structure contours represent approximate elevation of the base of the Mississippian limestone above sea le
at the surface; areas with strokes and dots represent exposures of crystalline r

The diagrams probably show the conditions as plainly as words can express them, but a few points should be emphasized. One point is that notable currents are not established in the limestones until the overlying Pennsylvanian shale has been removed. The first currents set up at the edge of the shale are ascending currents. Where the shale is cut through the currents are necessarily ascending until erosion of the surrounding country has lowered the groundwater table below the junction of the underlying limestones with the Pennsylvanian shale. Another point brought out by inspection of the diagrams is that water which has entered the circulation on the summit of the dome, has penetrated deeply into the stratified rocks, and has risen to the surface again will not be likely to penetrate so deeply a second time. This is equivalent to saying that water entering the strata on the outcropping edges flows along the bedding more easily than it penetrates the underlying strata. The effect is to concentrate in the upper circulation any mineral matter taken into solution by the water during its passage through the rocks.

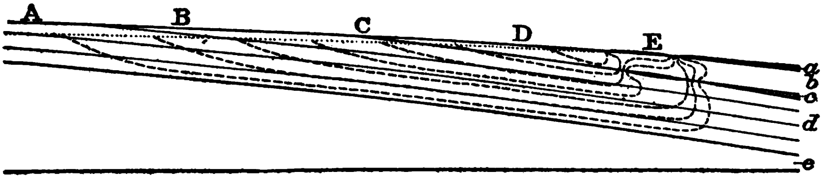


FIGURE 5.—Diagram showing late stage in Ozark artesian circulation. A–E, Stages in erosion of Pennsylvanian shale. *a*, Pennsylvanian shale; *b*, Mississippian limestone; *c*, Chattanooga (Devonian) shale; *d*, Ordovician and Cambrian rocks; *e*, pre-Cambrian rocks.

FLOWING WELLS.

The distribution of the flowing wells about the dome (Pl. IV) is just what should be expected from the foregoing discussion. The flowing wells in Missouri are in a circle that borders the uplift from St. Louis to the southwest corner of the State, either in the bordering area of Pennsylvanian rocks or in the adjoining zone of the uplift. The central part of the dome yields no wells that flow at the surface. In southeastern Kansas and northeastern Oklahoma there are flowing wells near the border of the uplift, but along all the southern border of the uplift there are only one or two flowing wells. The reasons for this absence of flowing wells are not far to seek; first, the limestone area north of the Boston Mountains is so well supplied with large springs of pure water that there has been no necessity for sinking deep wells; second, in the valley of the Arkansas, south of the Boston Mountains, where the surface water supply would render artesian water desirable, the depth to the water-bearing sandstones of the Cambrian and Ordovician rocks is too great to induce the boring of such wells.

GENESIS OF THE ORES.

GENERAL RELATIONS OF THE JOPLIN ZINC AND LEAD DEPOSITS.

The lead and zinc deposits of the Mississippi Valley occur in three groups: (1) Those of the Ozark region; (2) those of the upper Mississippi Valley, including the deposits of southern Wisconsin, eastern Iowa, and northern Illinois; and (3) those of outlying districts, including the central Kentucky, the Kentucky-Illinois, the southern Arkansas, and the Arbuckle Mountain, Okla., districts. The deposits of the Ozark region are by far the most important.

The Ozark region contains four districts: The southeastern Missouri disseminated lead district; the central Missouri district, characterized by small ore bodies yielding both lead and zinc; the Joplin or southwestern Missouri district, the main zinc-producing area; and the northern Arkansas district, producing chiefly zinc. These four districts are arbitrarily so chosen as to include the chief ore-producing centers. If all the scattered lead and zinc deposits known in the region were included, a continuous zone (except for the break between Miami, Okla., and Fayetteville, Ark.) would be outlined, beginning with the southeastern Missouri district on the east, thence circling to the northwest, thence to the south, not far from the margin of the Ozark uplift, and finally extending eastward along the northern slopes of the Boston Mountains.

Two forms of the iron-ore deposits of Missouri—the secondary limonite deposits and the hematites of the filled sinks—were originally deposited as sulphides. These deposits, which in the opinion of the writer are genetically related to the lead and zinc deposits, are practically confined to the area occupied by the Cambrian and Ordovician rocks and are most plentiful in the central and southern parts of this area.

The lead and zinc deposits of the Mississippi Valley are distinguished from one another by certain differences in the form and structure of the ore bodies and in the mode of occurrence and character of the ore. The Joplin district is characterized by the absence of well-defined fissures and by the common occurrence of the ores in large elongate bodies of generally slight horizontal extent, known as "runs," or in comparatively thin tabular bodies of great horizontal extent, known as "blanket breccias" or "sheet ground." The ores consist of zinc and lead sulphides, which occur in the runs mainly as a cement to chert breccias and in the sheet ground mainly as jasperoid replacements in horizontal layers between slightly disturbed beds of chert.

VERTICAL DISTRIBUTION OF THE JOPLIN ZINC AND LEAD DEPOSITS.

In connection with the descriptions of the different geologic formations in the district given in the chapter on areal geology the most productive ore horizons were pointed out, but for convenience they may be briefly summarized here, beginning with the uppermost.

1. The highest ore horizon stratigraphically lies in the rocks of Chester age immediately beneath the Pennsylvanian shale, and extends downward into the Boone formation. Ores from this horizon have been mined extensively at Miami, Okla., and drilling has shown that similar deposits extend northeastward into Kansas.

2. The great horizon of the "open-ground" or "confused-ground" deposits of the Joplin region is in that part of the Boone formation which lies above the Grand Falls chert member. These deposits were the first mined and they have yielded the great bulk of the ores so far produced by the district. A few of these deposits extend downward through the Grand Falls chert where the "open ground" cuts through that member, but generally where the deposits reach as deep as the upper surface of the Grand Falls chert that member terminates the ore and becomes the "bedrock."

3. The "sheet ground" of the region is formed in the upper part of the Grand Falls chert. This horizon has been productive in places at Galena, in Kansas, and in the territory immediately west of Joplin, in the area reaching from Oronogo to Duenweg, at Granby, and at Pioneer, in Missouri.

4. Disseminated and "open-ground" deposits of zinc and lead occur in that part of the Boone below the Grand Falls chert member, in rocks of Kinderhook age. These deposits have been opened at, Galena, Kans., and at Hornet, Granby, Oronogo, Stotts City, McDowell, and Aurora, Mo.

5. A fairly persistent ore horizon at the level of the Chattanooga (Devonian) shale has been demonstrated by a drilling campaign at Granby, Mo. No shaft has as yet been sunk to these deposits.

6. Some ore has been mined in the Sand Ridge mine at Aurora, Mo., below the horizon of the Chattanooga shale in rocks that probably belong to the Jefferson City limestone of Ordovician age. Ore below the horizon of the Chattanooga shale has also been reported in drilling in the Joplin region a number of times.

HISTORICAL OUTLINE OF VIEWS OF THE ORIGIN OF THE JOPLIN ORES.

If considered as to their genesis, the zinc and lead deposits of the Joplin district have long been acknowledged to be among the most puzzling in the whole category of ore deposits, and this statement is easily borne out by a perusal of the diverse views set forth in the following brief résumé of the various theories presented to account for their deposition:

Schmidt and Leonhard,[1] who were the first geologists to make a detailed investigation of the zinc and lead deposits of southwestern Missouri, concluded as the result of their studies that the ores were deposited contemporaneously with the dolomitization of the Mississippian rocks, apparently by laterally moving but not surface solutions.

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[1] Schmidt, Adolph, and Leonhard, Alexander, The lead and zinc regions of southwest Missouri: Missouri Geol. Survey Rept. 1873–74, pp. 412–414, 1874.

Jenney,[1] studying the deposits 20 years later, held that the ores were derived from the pre-Cambrian crystalline rocks through fissures of indefinite vertical extent and were deposited by solutions of moderate or normal temperature, cooled by the long journey from their sources. E. M. Shepard,[2] discussing the Greene County deposits a few years later, concurred in this view.

F. L. Clerc,[3] in a short description of the geology of the mines of the district, suggested that the ores were leached from the sink-hole [Cherokee] shale patches which dot the region and which "may be only a small part of those that once existed."

Haworth,[4] writing in 1904 upon field work done in 1898–99, concluded that the ores were in the main derived from the overlying Cherokee (Pennsylvanian) shale, and carried down and concentrated in the Mississippian limestones and cherts.

Buckley and Buehler,[5] in their report on the geology of the Granby area, state their belief that the metals of the present concentration were disseminated in the overlying Pennsylvanian shale, during the erosion of which the metals were oxidized and taken into solution, carried downward into the Mississippian limestones and cherts, and there concentrated and deposited by the mingling of oxidizing and reducing solutions.

Winslow [6] showed by the large-quantity analyses of Robertson that zinc and lead are disseminated through the Archean, Cambrian, Ordovician, and Mississippian rocks of the Ozark region, and he argued that these rocks by their decomposition in turn furnished the metals for the succeeding rocks; that the caverns and sink-hole breccias of the pre-Pennsylvanian erosion furnished favorable sites; that the solutions from the limestone land furnished the metals, and that the organic matter deposited by the Pennsylvanian sea constituted a suitable precipitant; wherefore he held that beneath the margin of the Pennsylvanian sea the conditions were most favorable for the concentration of the ores. With this view Branner [7], Keyes,[8] and Adams[1] are in substantial agreement, though Branner thinks that a part of some of the bedded deposits is of contemporaneous sedimentation with the inclosing rocks. Branner and Keyes also lay special stress on synclinal structure as favorable to the concentration of ore bodies.

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[1] Jenney, W. P., The lead and zinc deposits of the Mississippi Valley: Am. Inst. Min. Eng. Trans., vol. 22, pp. 219–224, 1894.

[2] Shepard, E. M., Geology of Greene County: Missouri Geol. Survey, vol. 12, pp. 169–173, 1898.

[3] Wilson, J. N., Lead and zinc ore of southwest Missouri mines; authenticated statistics, with contributions by F. L. Clerc and T. N. Davey, Carthage, Mo., pp. 8–11, 1887.

[4] Haworth, Erasmus, Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, pp. 117–126, 1904 (distributed 1907).

[5] Buckley, E. R., and Buehler, H. A., Geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, pp. 78–110, 1906.

[6] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 477–487, 1894.

[7] Branner, J. C., The zinc and lead region of north Arkansas: Arkansas Geol. Survey Ann. Rept. for 1892, vol. 5, pp. 15–35, 1900.

[8] Keyes, C. R., Diverse origins and diverse times of formation of the lead and zinc deposits of the Mississippi Valley: Am. Inst. Min. Eng. Trans., vol. 31, pp. 607–611, 1902; Ozark lead and zinc deposits: their genesis, localization, and migration: Am. Inst. Min. Eng. Trans., vol. 40, pp. 184–231, 1910.

Bain[2] adopted the theory, previously worked out by Van Hise for the upper Mississippi Valley region, of a primary deposition by ascending artesian currents and a secondary concentration by descending currents keeping pace with the lowering of the land level by erosion. Bain further contributed the view that the ore-bearing currents in the Joplin region ascended from the Cambrian and Ordovician rocks through fault zones cutting the "Devono-Carboniferous" shales, thus accounting for the localization of the ores and the occurrence of dolomite.

In the Joplin district folio[3] Smith accepted, with modifications, the Van Hise-Bain idea of a primary concentration of the ores by ascending waters that had derived their metal content from either the Mississippian or the Cambrian and Ordovician limestones, although convincing evidence was not at hand to decide from which source the metals were chiefly derived. He greatly minimized the importance of sulphide enrichment by downward currents, maintaining that the vertical order, frequently observed, of galena above, next blende, with iron sulphide in depth, is one normal to primary deposition by ascending solutions. In the chapters on stratigraphic and structural geology in that folio the junior author (the present writer) showed that only minor faulting was found in the area under discussion and pointed out that the Chattanooga (Devonian) shale was not persistent and hence not a complete barrier to the ascent of solutions from the Cambrian and Ordovician rocks.

The writer, in the present paper, still maintains that the rocks of Kinderhook age—that is to say, the lower part of the Boone formation—even in their more shaly phases are, nevertheless, decidedly arenaceous and are not an effective barrier to the ascent of the ore-bearing solutions from the Cambrian and Ordovician limestones below. This view he holds to be proved by the finding of ore rich enough to justify mining at places in those rocks, notably at Springfield, Aurora, McDowell, Stotts City, Joplin, Hornet, and Galena. He further holds that the Chattanooga (Devonian) shale is an effective barrier to the ascent of the solutions, as is proved by the absence of ore bodies over the known distribution of that formation as shown on the map (Pl. III). The writer also believes that, directly or indirectly, the Cambrian and Ordovician limestones and dolomites have furnished the major part of the ores now found in the Joplin district; that these ores were precipitated from ascending alkaline-saline sulphureted waters similar to those now rising in artesian wells within the Pennsylvanian area immediately west of the Joplin district; that the pyrite and marcasite deposits which gave rise to the secondary limonite deposits and the hematite deposits in the filled sinks of the Cambrian and Ordovician area are of similar origin to the lead and zinc deposits; that the solution, transfer, and redeposition of sulphides by such solutions is simple, as is shown in the chapter on the chemistry of lead and zinc compounds; that such metals as are carried by sulphate acid waters in the district have resulted from oxidation of the ore deposits and represent merely a local transfer of such metals; that the deeper waters of the district now carry less mineral matter in solution—that is, less salts of the alkalies and metals—than formerly because they have been "sweetened" by long-continued circulation, whereas the artesian waters drawn from the same horizons west of the Joplin district have preserved their pristine character because they have been impounded beneath the Pennsylvanian shales; all of which beliefs the writer holds are substantiated by the facts herein set forth.

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[1] Adams, G. I., Zinc and lead deposits of northern Arkansas: U. S. Geol. Survey Prof. Paper 24, pp. 43–46, 1904.

[2] Bain, H. F., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-Second Ann. Rept., pt. 2, pp. 204–215, 1901.

[3] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), pp. 18–19, 1907.

It will be observed that in the foregoing views the rocks at practically all geologic horizons in the area have been drawn upon as sources of mineralization, namely, the pre-Cambrian, Cambrian and Ordovician, Mississippian, and Pennsylvanian. This paper will be confined to an endeavor to show that the ores were derived chiefly from the Cambrian and Ordovician rocks and will not attempt to discuss even obvious objections to other conclusions unless such discussion appears necessary to elucidate points in connection with the view that the ores were deposited by ascending circulating artesian waters.

CHEMISTRY OF LEAD AND ZINC SOLUTIONS.

NATURE OF ORE SOLUTIONS.

Ore solutions, which are in general dilute solutions charged with divers metallic salts in various degrees of concentration, are regarded by the physical chemist as complex but homogeneous systems in which the salts are dissociated in various degrees of ionization and hydrolyzation and in which the acid and base radicles exist in all possible combinations as well as in individual ions, the relative quantity of each depending on the ionization constants, the solubility products, and the original concentration of the salts. This view no doubt presents a true picture of the actual constitution of an ore solution, but for the purposes of this discussion it will be preferable to regard an ore solution as a mixture of various simple salt solutions, the reactions of each of which may be considered separately. As the ionized radicles in a salt solution are balanced against one another in harmonious equilibrium, the violence done to the physico-chemical conception by thus treating the ore solution as a mixture of simple solutions is more apparent than real.

In this paper it will be assumed that the metals of the ores were originally disseminated through the limestones as sulphides, and an attempt will be made to picture the solution of these sulphides, their transportation, and their redeposition.

SOLUTION AND TRANSFER AS SULPHATES.

The sulphides of the metals coming in contact with air or oxidizing solutions are changed to sulphates, the end results being expressed by the following reactions:

$$PbS + 4O = PbSO_4$$
$$ZnS + 4O = ZnSO_4$$
$$FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$$

The sulphates of the metals, except that of lead, which is moderately insoluble, are readily soluble and enter into the general ground-water circulation. The metals are transferred in quantity as sulphates probably for short distances only. As shown farther on (pp. 55–56) zinc sulphate in an underground circulation carrying earthy bicarbonates, organic matter, carbon dioxide, and hydrogen sulphide may react with the earthy bicarbonates and remain in solution to a small extent as zinc bicarbonate or, according to Bailey (see p. 69), it may be precipitated as zinc carbonate; or it may react with the limestone country rock and form zinc carbonate, thus:

$$ZnSO_4 + CaCO_3 = ZnCO_3 + CaSO_4$$

or (see pp. 62–66) it may be reduced by organic matter and be deposited as the sulphide:

$$ZnSO_4 + CH_4 = ZnS + 2H_2O + CO_2$$

or, as shown by Bischof,[1] it may be precipitated as the sulphide by hydrogen sulphide, thus:

$$ZnSO_4 + H_2S + CaCO_3 = ZnS + CaSO_4 + CO_2 + H_2O$$

In mines that contain considerable iron pyrites and that are alternately dry and wet there is likely to be rapid oxidation. If the water from such a mine does not come in contact with limestone it is likely to be heavily charged with the sulphates of the metals. For the reasons pointed out this transfer is likely to be of limited horizontal extent, in general from upper to lower levels in the mine. The few scattered "buttermilk" springs of the district, which carry large quantities of zinc sulphate, mark the outcrop of exclusively cherty strata which have elsewhere received either mine drainage or drainage from oxidizing sulphide ore bodies that has not been neutralized by contact with limestone. (See analysis No. 116 in the synoptical table.) The "alum" springs similarly mark the emergence of drainage from sulphide deposits undergoing oxidation. (See analyses Nos. 117 and 118.)

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[1] Bischof, Gustav, Elements of chemical and physical geology (translation by B. H. Paul and J. Drummond), vol. 1, p. 15, London, Cavendish Society, 1854.

As before stated, the transfer of the metals as sulphates in quantity probably covers short distances only. Few if any of the analyses of deep waters fail to reveal the presence of more or less sulphate radicle. If such waters carry traces or measurable quantities of zinc, one can not say that the ionized solution does not carry potential zinc sulphate. Minute quantities of the metallic sulphates may therefore, in effect, be carried for long distances.

Gottschalk and Buehler[1] have made and published a series of important experiments to show the order of oxidation of the sulphides. They found that the natural sulphides show differences in conductivity and may be arranged in a series analogous to the electromotive series of the metals. In moistened contact in pairs they act as batteries; the mineral that stands lower in the electromotive series is dissolved, and the mineral that stands higher is protected from oxidation. The following measurements of the conductivity of minerals have been taken from the much fuller table in the more recent of the two articles cited. The measurements are in volts and are made against a copper wire.

Table of conductivities of natural sulphides.

	Volt.
Marcasite	+0.37
Chalcopyrite	+0.18 to + .30
Pyrite	+ .18
Galena	+ .15
Metallic copper	.00
Sphalerite	− .2 to − .4

In accordance with this series we should expect, as pointed out by the authors cited, that with galena and sphalerite in contact in oxidizing waters, the galena would be preserved at the expense of the sphalerite; and that, with pyrite or marcasite in contact with either galena or sphalerite, the lead or zinc sulphide would go into solution, leaving behind the iron sulphide. As a matter of fact, this is what happens, both in the laboratory and in the field. The laboratory experiments showed that marcasite in contact with sphalerite dissolved only one-sixth to one-fourth as rapidly as when

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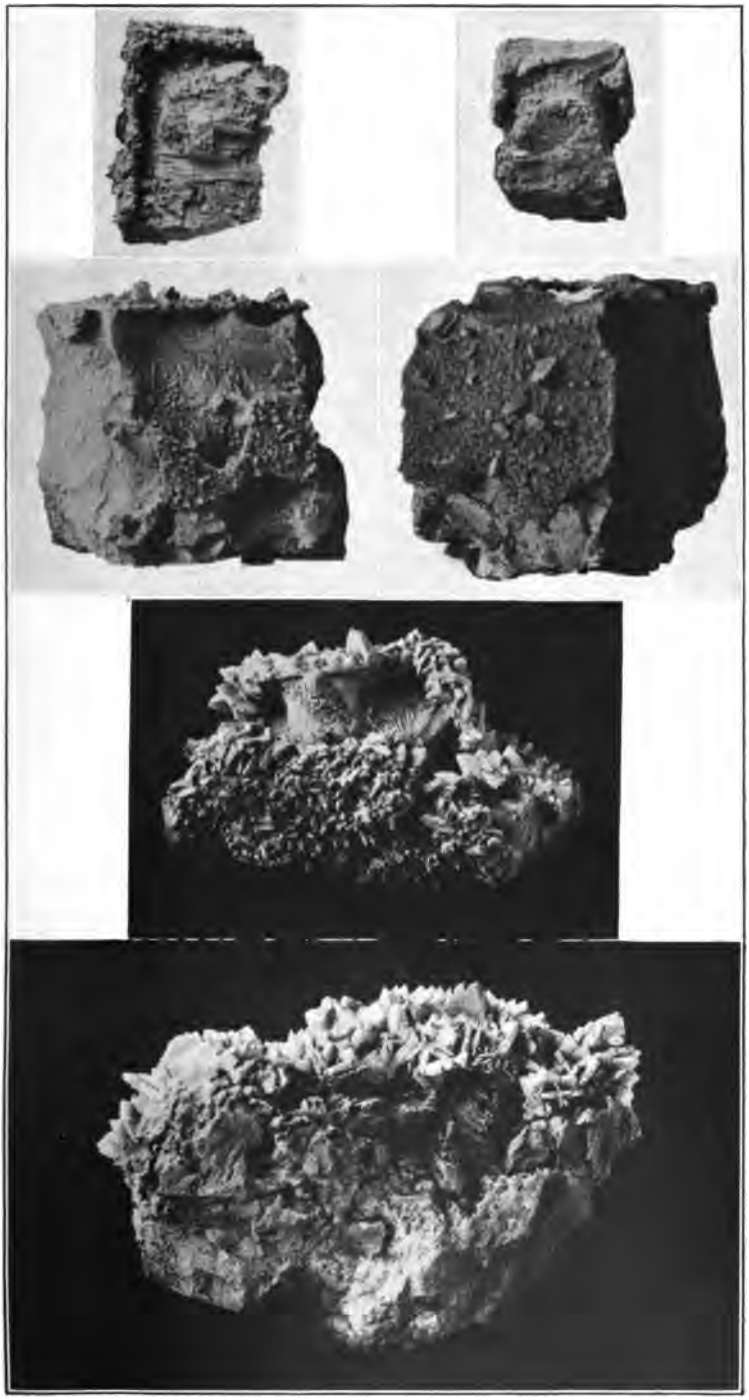
[1] Gottschalk, V. H., and Buehler, H. A., Economic geology, vol. 5, pp. 28–35, 1910; vol. 7, pp. 15–34, 1912.



SPECIMENS OF SPHALERITE AND GALENA ETCHED FROM BENEATH A CRUST OF MARCASITE AND PYRITE.

The five upper specimens show etched galena; the lower specimen shows etched sphalerite.

alone, and marcasite in contact with galena dissolved only one forty-fourth to one-sixteenth as rapidly as when alone. In the same experiments the sphalerite in contact with marcasite dissolved 10 to 14 times as fast as when alone and the galena in contact with marcasite dissolved 6 to 14 times as fast. This action is analogous to the electrolytic action by which the zinc coating protects the iron in galvanized iron. In the field in the Joplin district the writer has seen marcasite incrusting crystals and surfaces of both galena and sphalerite and continuing beyond their present limits, thus marking former extensions of those faces that have been etched away, leaving the unaltered marcasite crusts. Plate V shows a specimen of sphalerite and several specimens of galena etched from beneath a crust of marcasite. The marcasite is bright and fresh and some individual crystals of it that extend inward beyond the plane of former faces of galena or sphalerite suggest that marcasite has to a small extent been deposited since the zinc and lead sulphides were carried away. Evidence of this sort of action is most clearly presented in the sheet ground of the district, where, owing to its depth below the surface and below the normal groundwater level, oxidation and solution have not gone beyond the capacity of the zinc and lead sulphides to protect the marcasite. Nearer the surface, and above the ground-water level, oxidation and solution have generally reached the stage where all three sulphides are gone. Moreover, the necessary condition of moist contact of the sulphides may not exist in many of the shallower deposits. Again, the galena in this situation protects itself by forming an enveloping film of lead carbonate. Hence the shallower deposits may yield galena that is practically free from sphalerite and marcasite.

On the other hand, the writer has seen cubes of galena from the 230-foot level of the Sullivan mine, at Miami, which were covered with a thin crust of small ruby crystals of sphalerite and in which the galena plainly had been etched from beneath the sphalerite. Close examination showed that a little pyrite was dusted between the galena and the sphalerite. With pyrite-galena forming one couple and pyrite-sphalerite another couple, it may be that the greater mass of the galena operated to cause it to go into solution faster than the sphalerite. In the mines there usually does not seem to be much difference in the etching of adjacent galena and sphalerite.

Fox,[1] in 1830, while working on electric currents developed between separate parts of metalliferous veins, investigated the conductivity of the minerals of the veins and published a table which in sequence agrees in essential particulars with the one cited above. A little more than 40 years later, Skey,[1] while engaged in a study of the amalgamation of gold ores, discovered independently the voltaic relations of the sulphide minerals and gave a table of their relative conductivities very similar to the table prepared by Fox.

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[1] Fox, R. W., On the electromagnetic properties of metalliferous veins in the mines of Cornwall: Roy. Soc. London Philos. Trans., pt. 1, pp. 399–414, 1830.

Gottschalk and Buehler, in their measurements of the electromotive force of the minerals, immersed them in distilled water. They noted that the potential of some minerals (of sphalerite, for instance) paired with pyrite was at first high, but that it dropped to one-tenth in a few seconds. Wells,[2] who has more recently studied the electrochemical activity of certain ore minerals, finds that the potential developed, depending as it does upon the oxidation of one of the minerals, varies with the mineral, with the character of the solution, and with the length of time covered by the experiment. As these are factors that would enter into any ore deposition it is obvious that the data which Wells gives represent more nearly the natural conditions. Gottschalk and Buehler give the order of initial potential in distilled water, whereas Wells gives the order in various solutions after action has gone on for some time. However, the order of the ore minerals with which we are here concerned is the same in both tables, though the spacing may be somewhat different, and consequently it will not be necessary to pursue the comparison further.

SOLUTION AND TRANSFER AS CHLORIDES.

The solubility in water of certain haloid compounds of zinc, notably the chloride, the bromide, and the iodide, is remarkably high, the quantities of the anhydrous salt of these compounds held in solution by 1 liter of water at 18° C. being, respectively, 2,039, 4,782, and 4,190 grams.[3] In contrast with these, the solubility of the equivalent lead compounds is 14.9, 5.98, and 0.8 grams, respectively. The solubility of the compounds of lead and zinc, and in particular of the sulphides of those metals, in saline solutions of the alkalies and alkaline earths is quite another matter, however; and it is with the solubility of the metallic sulphides that we are concerned.

Lindgren[4] has this to say relative to the transportation of lead as the chloride:

> Galena, on the other hand, is one of the most insoluble sulphides. It is said to be slightly soluble in water and also in solutions of sodium sulphides.[5] Lead sulphate,

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[1] Skey, William, On the capability of certain sulphides to form the negative pole of a galvanic circuit or battery: New Zealand Inst. Trans. and Proc., vol. 3, pp. 222–225, 1871; and On the electromotive power of metallic sulphides: Op. cit., pp. 232–236.

[2] Wells, R. C., Electrochemical activity between solutions and ores: Econ. Geology, vol. 8, pp. 571–577, 1913; also Electric activity in ore deposits: U. S. Geol. Survey Bull. 548, 1914.

[3] Smith, Alexander, Introduction to inorganic chemistry, rev. ed., p. 544, New York, 1910.

[4] Lindgren, Waldemar, Mineral deposits, p. 415, New York, 1913.

[5] Doelter, C., Min. pet. Mitt., vol. 11, p. 319, 1890.

> according to Kohlrausch and Rose,[1] is soluble to the extent of 46 milligrams in 1 liter of pure water. The presence of free acids decreases the solubility. Chlorides are more effective. According to Fresenius lead sulphate is soluble in ferric chloride and sodium chloride decomposes it slowly. Becquerel found that 1 liter of saturated solution of sodium chloride dissolves 660 milligrams of $PbSO_4$ and in this condition it is probably converted to the much more soluble lead chloride by mass action. $PbCl_2$ is soluble in pure water at the rate of 0.909 per cent at 15° C., rising to 3.34 per cent at 100° C.;[2] a 5 per cent solution of sodium chloride, having a common ion, retards the solubility about one-fourth.
>
> From all this it appears probable that solutions of sodium chloride are the most effective carriers of lead * * * and in many cases at least such solutions mixed with sulphates probably were active in the genesis of these deposits [that is, lead and zinc deposits in sedimentary rocks]. * * * When such solutions encountered hydrogen sulphide or abundant organic matter precipitation of the lead as sulphide undoubtedly would follow.

But little data are at hand concerning the solubility of zinc sulphide in solutions of sodium chloride. In the experiment by Wells, detailed on page 58, the quantity of zinc dissolved by a solution of 1 gram of sodium chloride in a liter of water was a little less than half that dissolved by water saturated with hydrogen sulphide and less than one-sixth that dissolved by water saturated with carbon dioxide. Certain strong brines from Kentucky, to be noted later, show traces and measurable quantities of zinc, reported as the carbonate, however. Also the waters of the German springs, the Solquelle "Bonifazius"[3] and the Viktoriaquelle,[4] both nearly pure solutions of salt, contain respectively a trace and a measurable quantity of zinc.

SOLUTION AND TRANSFER AS SULPHIDES AND HYDROSULPHIDES.

Weigel[5] gives a table showing the solubility in pure water of various crystalline metallic sulphides, as determined by the conductivity of the solution, and from this table are taken the data relative to the sulphides with which we are concerned.

Solubility of crystalline sulphides in pure water at 18° C. (65° F.).

	Gram-mol per liter.	Grams of mineral dissolved per liter of water.
Galena, from Freiberg	1.21×10^{-6}	0.00029
Galena, artificial	1.21×10^{-6}	.00029
Cuprous sulphide, regular	3.1×10^{-6}	.00049
Sphalerite, artificial	6.63×10^{-6}	.00065
Sphalerite, from Santander	6.65×10^{-6}	.00065
Greenockite	8.99×10^{-6}	.00130
Millerite	16.29×10^{-6}	.00148
Wurtzite	28.82×10^{-6}	.00281
Pyrite, artificial	40.84×10^{-6}	.00490
Pyrite, from Freiberg	48.89×10^{-6}	.00587

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[1] Kohlrausch, F., and Rose, F., Zeitschr. physikal. Chemie, vol. 12, p. 241, 1893.

[2] Landolt and Börnstein, Physikalisch-chemische Tabellen, Berlin, 1905.

[3] Analysis No. 29 in the synoptical table, p. 150.

[4] Analysis No. 50 in the synoptical table, p. 150.

[5] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, p. 293, 1907.

It will be observed that sphalerite is much more soluble than galena and ranks between galena and pyrite. Field experience in general corroborates Weigel, though of course the conditions are not exactly parallel, as oxidation enters into the solution of the sulphides under field conditions in the superficial zone. On the other hand, under some conditions, as shown by the example cited on page 45, galena appears to be less resistant than sphalerite, for it has been etched from beneath a crust of that mineral.

Becker and Melville investigated the solubility of various sulphides in solutions containing sodium sulphide and sodium hydroxide. The results as regards sphalerite and galena are as follows:

> A solution containing a little less than 1,000 parts of Na_2S and about 100 parts of NaHO dissolved 1 part of ZnS at 20°. The sulphydrate dissolves only a very small quantity of zinc sulphide. Sodic carbonate partially saturated with sulphydric acid also dissolves zinc sulphide. Over 1,000 parts of neutral sodium carbonate which had been semisaturated with hydrogen sulphide were found necessary to dissolve 1 part of zinc sulphide at 20°. * * *
>
> The sulphides of lead and silver seem to be entirely insoluble in solutions of sodic sulphide, of sodic sulphydrate, or in solutions of sodic carbonate partially saturated with hydrosulphuric acid. We have obtained no evidence of solution with these sulphides even when heated above 100° with the reagents in closed tubes.
>
> The foregoing experiments show that there is a series of compounds of mercury of the form HgS, nNa_2S one or the other of which is soluble in aqueous solutions of caustic soda, sodic sulphydrate, or sodic sulphide, and apparently also in pure water, at various temperatures. These solutions subsist, or subsist to some extent, in the presence of sodic carbonates, borates, and chlorides. * * * Bisulphide of iron, gold, and zincblende form double sulphides with sodium, which appear to be analogous to those of mercury. Copper also forms a soluble double sulphide, but combines more readily with sodic sulphydrate than with the simple sulphide. All of these soluble sulphosalts may exist in the presence of sodic carbonates.[1]
>
> When hydrogen sulphide is passed through waters containing neutral carbonate at ordinary temperatures the following reaction is known to take place: $Na_2CO_3+H_2S=NaHCO_3+NaHS$; so that, if the solution of the neutral carbonate be moderately strong, a portion of the less soluble acid carbonate is precipitated by hydrogen sulphide. If hydrogen sulphide be passed through the solution until it is only semisaturated or if a saturated solution be added to a solution of the neutral carbonate, the composition will be $Na_2CO_3+NaHCO_3+NaHS$.[2]

In this connection attention is called to the fact that nearly half the Kentucky waters which contain hydrogen sulphide contain also sodium sulphide, and that of the 89 waters yielding zinc (see p. 92), 36 contain hydrogen sulphide, and of these 17 are reported to contain sodium sulphide. The waters from the Whitaker well at Pryor Creek, Okla., and from the waterworks well at Pittsburg, Kans., both in the Ozark region, contain alkaline sulphides, and probably many other of the sulpho-saline waters of the district and of the region immediately west of it also contain alkaline sulphides.

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[1] Becker, G. F., Natural solutions of cinnabar, gold, and associated sulphides: Am. Jour. Sci., 3d ser., vol. 33, p. 208, 1887.

[2] Becker, G. F., Geology of the quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, p. 427, 1888.

Many of the waters considered in the table of analyses given in this paper (pp. 107–146) contain alkaline and earthy bicarbonates and hydrogen sulphide, and if they contain these they probably contain also more or less sodium sulphide or similar alkaline-earth sulphides, as indicated by the following reactions:

$$Ca(HCO_3)_2 + 2NaCl + H_2S = Na_2S + CaCl_2 + 2H_2O + 2CO_2$$
$$2NaH(CO_3) + H_2S = Na_2S + 2H_2O + 2CO_2$$
$$Ca(HCO_3)_2 + H_2S = CaS + 2H_2O + 2CO_2$$

In the presence of hydrogen sulphide sodium sulphide forms the hydrosulphide, as shown by this equation:

$$Na_2S + H_2S = 2NaHS$$

Concerning the action of sodium sulphide and hydrosulphide on zinc salts Thomsen[1] has this note [translated and equations supplied by the present writer]:

> When a dilute solution of zinc sulphate is treated with an equivalent of sodium sulphide solution, a precipitate is formed which contains all the zinc and all the sulphur, leaving a neutral solution of sodium sulphate [$ZnSO_4 + Na_2S = ZnS(xH_2O) + Na_2SO_4$]; the precipitate is hydrous zinc sulphide. When the zinc sulphate solution is precipitated by an equivalent of sodium hydrosulphide solution, the decomposition is also complete; the precipitate contains the whole of the zinc, and the solution reacts weakly acid [$ZnSO_4 + 2NaHS = Zn(HS)_2 + Na_2SO_4$]; the precipitate is apparently zinc hydrosulphide. When, however, a zinc sulphate solution is treated with a double quantity of the solution of sodium hydrosulphide, there is no precipitate, but a clear or weakly opalescent fluid [$ZnSO_4 + 4NaHS = Na_2ZnS_2 + Na_2SO_4 + 2H_2S$]. The solution yields, with sodium hydroxide and with acids, a precipitate of zinc sulphide, or more probably zinc hydrosulphide. After standing for a few hours there gradually forms in the solution a slimy precipitate, but this is redissolved on heating the solution.
>
> The behavior of the zinc-sulphate solution toward sodium hydrosulphide is, therefore, strictly analogous to its behavior toward sodium hydroxide; for an equivalent quantity of sodium hydroxide decomposes the zinc sulphate solution completely, with the formation of a precipitate of zinc hydroxide, whereas an excess of sodium hydroxide gives a clear solution containing zinc oxide-sodium hydroxide [Na_2ZnO_2= sodium zincate]. Zinc hydrosulphide is soluble in sodium hydrosulphide just as hydrated zinc oxide is soluble in sodium hydroxide.

The very similar calcium hydrosulphide may be formed directly from calcium carbonate and hydrogen sulphide, as shown by Béchamp[2] in the reaction:

$$2CaCO_3 + 2H_2S = Ca(HCO_3)_2 + Ca(HS)_2$$

The efficacy of calcium hydrosulphide in the solution and transportation of zinc is considered on page 58.

Another set of conditions that must be brought about to some extent in the deep waters of the Joplin district in their circulation through the limestones would give opportunity for the action of sodium sulphide or sodium hydrosulphide (and also of the alkaline-earth sulphides and hydrosulphides) on zinc sulphide. These waters contain, among other constituents, sodium chloride and hydrogen sulphide in relative abundance. The sodium chloride will be almost completely ionized, but the weaker hydrogen sulphide will be ionized to a small extent only, the quantities of the nonionized compounds, of the ion combinations, and of the free ions depending on the ionization constants of sodium sulphide and sodium hydrosulphide and the concentrations of the original salts and on the solubility products of the insoluble salts. We should expect a system to be formed such as the following:

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[1] Thomsen, Julius, Notes on zinc sulphydrate: Chem. Gesell. Ber., vol. 11, pt. 2, p. 2044, 1878.

[2] Béchamp, A., Recherches sur l'état du soufre dans les eaux minérales sulfurées; essai sur l'une des causes probables de la formation de ces eaux: Annales chim. et phys., 4th ser., vol. 16, p. 202, 1869. Quoted by Chase Palmer in U. S. Geol. Survey Bull. 340, p. 455, 1908.

$$NaCl + Na^+ + Cl^- + Na_2S + NaHS + HCl + H^+ + S^{--} + H_2S$$

If this solution percolating through the limestones encounters disseminated zinc blende or galena, we should expect the sodium sulphide or the sodium hydrosulphide to link itself to the lead or zinc sulphide in some combination of double sulphides which is soluble and thus carry it into the solution. When the solution eventually reaches the surface a part of the nonionized or free hydrogen sulphide will escape. The concentration of the free hydrogen sulphide having been thus lowered, equilibrium will be restored by the withdrawal of a part of the ionized hydrogen sulphide from the system, its withdrawal breaking up a part of the alkali sulphide and hydrosulphide and resulting in the precipitation of zinc blende or galena. In this, as in other reactions which depend on the participation of hydrogen sulphide, the effectiveness of the reaction will vary as the quantity of hydrogen sulphide in solution, which may undoubtedly be large in the deep waters, since the hydrogen sulphide is set free in depth, where the water will have great capacity for holding the gas in solution on account of the hydrostatic pressure. As such solutions approach the surface, and the pressure grows less, the hydrogen sulphide will escape, the result being a readjustment of equilibrium by the splitting up of the soluble sulphides and the deposition of the simple sulphides.

SOLUTION AND TRANSFER AS DISPERSED COLLOIDAL SULPHIDES.

Tolman and Clark[1] have recently presented experimental evidence to show that hydrogen sulphide and carbon dioxide are very effective dispersing agents for copper sulphides. Hydrogen sulphide and carbon dioxide are universally present in the deep-well waters of the Joplin region, the latter in greater abundance than the former. If the dispersing power of these agents should be found to extend to the sulphides of lead and zinc, it would apparently offer a simple method of explaining the transportation and deposition of the metals of the Joplin zinc and lead deposits, as we have only to conceive the sulphides of those metals taken into colloidal suspension in the underground water through the action of carbon dioxide and hydrogen sulphide, carried to the surface by the artesian circulation, and there precipitated by the escape of the gaseous dispersing agents.

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[1] Tolman, C. F., and Clark, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions and the dispersion and precipitation of copper sulphides from colloidal suspensions, with a geologic discussion: Econ. Geology, vol. 9, pp. 559-592, 1914. Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., vol. 1, No. 1, pp. 75-150, 1914.

However, it remains to be seen whether the action exhibited in the simple solutions used in Clark's experiments is effective in such heterogeneous mixtures of very dilute salt solutions as the deep waters of the Joplin region. Moreover, most of those waters are in reaction nearly neutral, some being faintly acid and others faintly alkaline. Clark[1] says that the dispersion of sulphides is least in acid solutions and enormously greater in alkaline solutions. Therefore, effects comparable to the maximum results of his experiments are certainly not to be expected in the underground waters of the Joplin region. The same author[2] gives the results of several experiments upon colloidal copper sulphide in a $\frac{1}{1.400}$ normal solution of potassium carbonate and potassium chloride. When hydrogen sulphide was added the colloidal copper sulphide remained in suspension, but when carbon dioxide was added to another portion there was a clean-cut flocculation. Thus in an alkaline solution, which is the most favorable for dispersion, carbon dioxide caused flocculation. In the underground waters of the Joplin region, which were dilute, nearly neutral, containing chlorides of the alkalies and bicarbonates of the alkaline earths, and carbon dioxide in amount exceeding the hydrogen sulphide, it seems doubtful whether metals transported as dispersed colloidal sulphides have played any great part in the formation of the ore deposits. Other reasons leading to the same conclusion are given on page 167.

SOLUTION AND TRANSFER AS ZINCATES AND SULPHOZINCATES.

Soluble sodium zincate is formed by the action of an excess of sodium hydroxide upon zinc sulphate, thus:

$$ZnSO_4 + 2NaOH = Na_2ZnO_2 + H_2SO_4$$

The same compound may be formed by the action of sodium bicarbonate on zinc sulphide, thus:

$$ZnS + 2NaHCO_3 = Na_2ZnO_2 + H_2S + 2CO_2$$

As calcium bicarbonate is much more plentiful than sodium bicarbonate in the deep waters of the district, it will be more appropriate to write the equation for the similar calcium zincate thus:

$$ZnS + Ca(HCO_3)_2 = CaZnO_2 + H_2S + 2CO_2$$

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[1] Tolman, C. F., and Clark, J. D., op. cit., p. 132.

[2] Idem, p. 141.

Thomsen[1] noted that soluble sodium sulphozincate is formed by the action of sodium hydrosulphide upon zinc sulphate according to the reaction:

$$ZnSO_4 + 4NaHS = Na_2ZnS_2 + Na_2SO_4 + 2H_2S$$

It seems likely that sodium sulphozincate may be obtained directly from sphalerite by sodium hydrosulphide according to the equation:

$$ZnS + 2NaHS = Na_2ZnS_2 + H_2S$$

With the escape of hydrogen sulphide at the surface, the sodium sulphozincate would split up into sodium sulphide and zinc sulphide, and the latter would be precipitated.

Similarly calcium sulphozincate may be derived from sphalerite by the following reaction:

$$ZnS + Ca(HCO_3)_2 + H_2S = CaZnS_2 + 2H_2O + 2CO_2$$

It will be shown later that sphalerite is dissolved as the bicarbonate by the artesian circulation with the liberation of hydrogen sulphide. Such a solution coming in contact with more sphalerite would fulfill the first half of the equation last given, and it is therefore reasonable to suppose that the metals may be in part transported as zincates and sulphozincates.

As the solutions approach the surface some of the carbon dioxide will escape, and in the subsequent readjustment both zincate and sulphozincate will be broken up, zinc sulphide and calcium carbonate (calcite) being deposited thus:

$$CaZnO_2 + H_2S + CO_2 = ZnS + CaCO_3 + H_2O$$
$$CaZnS_2 + H_2O + CO_2 = ZnS + CaCO_3 + H_2S$$

The deeper waters of the Joplin district circulating through the dolomitic limestones of Cambrian and Ordovician age take up so much magnesium that dolomite is to be expected rather than calcite as a result of the foregoing reactions. Calcite is a common gangue mineral in the Joplin district, but dolomite is so generally an accompaniment of the zinc deposits that it has passed into a miner's saying that "Spar [dolomite] is the mother of 'jack' [zinc blende]." Hence, a posteriori, one would be inclined to think the foregoing reaction would be effective in the genesis of the Joplin deposits.

SOLUTION AND TRANSFER AS CARBONATES AND BICARBONATES.

FORMATION OF THE CARBONATES AND BICARBONATES.

The carbonates of the metals may be formed by reaction of the sulphates of the metals with the earthy carbonates and bicarbonates, as shown in a preceding section, or they may be formed by solution of the sulphides in waters carrying carbonic acid according to the following reactions:

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[1] Thomsen, Julius, Notes on zinc sulphydrate: Chem. Gesell. Ber., vol. 11, pt. 2, p. 2044, 1878.

$$
\begin{aligned}
&PbS + CO_2 + H_2O = PbCO_3 + H_2S \\
&PbS + 2CO_2 + 2H_2O = Pb(HCO_3)_2 + H_2S \\
&ZnS + CO_2 + H_2O = ZnCO_3 + H_2S \\
&ZnS + 2CO_2 + 2H_2O = Zn(HCO_3)_2 + H_2S
\end{aligned}
$$

The carbonates of lead and zinc are soluble to a considerable extent in water, but the bicarbonates of these metals are many times more soluble than the carbonates. The experiments described below were performed by E. C. Sullivan in the chemical laboratory of the United States Geological Survey in order to obtain accurate data upon this point:

A weight of 5 grams of zinc carbonate (Schuchardt puriss.) was stirred in 1 liter of water several hours and filtered. The solution was evaporated and the zinc weighed as sulphate. The zinc sulphate found was equivalent to 0.0093 gram of zinc carbonate per liter in water.

A weight of 5 grams of zinc carbonate (Schuchardt puriss.) was taken in 1 liter of water, carbon dioxide was passed through, the mixture was stirred for some hours, and filtered at 12° C. The solution was evaporated and the zinc weighed as zinc sulphate. The sulphate found showed that 0.7797 gram of zinc carbonate had dissolved in 1 liter of water, equal to $\frac{1}{1282}$ of the weight of the water. Bischof[1] says that water saturated with carbonic acid dissolves $\frac{1}{4108}$ of its weight of artificial carbonate of zinc.

A weight of 0.5 gram of lead carbonate (c. p. Schuchardt) was taken in about 1 liter of CO_2-free water, the mixture stirred vigorously for one day and part of another and filtered at 7° C., ammonium sulphate was added, hydrogen sulphide passed into the solution, and the lead finally weighed as sulphate. The weight of the sulphate gave 0.0019 gram as the lead carbonate dissolved in 1 liter of water.

A weight of 0.5 gram lead carbonate (c. p. Schuchardt) was taken in about 1 liter of water, carbon dioxide passed into the mixture, with stirring several hours daily for four days; filtered at 13° C. Filtrate contained no chloride and no sulphate. Ammonium sulphate was added, hydrogen sulphide passed into the solution, and the lead finally weighed as sulphate. The lead found was equivalent to 0.0395 gram lead carbonate per liter.

These results corroborate the data quoted from Pleissner and Auerbach on pages 56–57 and show that, under the conditions of the experiment, zinc bicarbonate is 83.8 times as soluble as zinc carbonate and that lead bicarbonate is 20.8 times as soluble as lead carbonate. The value of the experiments with lead carbonate, however, is somewhat impaired by the greater length of time and the higher temperature involved in the solution as bicarbonate. These results indicate that, of the reactions mentioned at the beginning of this section, those yielding the bicarbonates would be the ones generally followed in the presence of a plentiful supply of carbon dioxide. Unless there is an excess of carbon dioxide (or bicarbonate radicle) over that needed to form normal carbonate, however, the hydrogen sulphide will precipitate the metals as sulphides.

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[1] Bischof, Gustav, Elements of chemical and physical geology (translated by B. H. Paul and J. Drummond), vol. 1, p. 15, London, Cavendish Society, 1854

Chase Palmer[1] has found by experiment that zinc will not be precipitated by hydrogen sulphide in the presence of sufficient carbon dioxide. A similar reaction for iron was long ago suggested by Peter,[2] who wrote:

> It is remarkable in regard to these waters [of the Estill Springs], as well as those of the Olympian Springs, and of several other springs of the State, that bicarbonate of soda appears to exist, in the recent waters, in solution with bicarbonate of lime, magnesia, and iron, even in the presence of a trace of sulphureted hydrogen. These substances being all held in harmonious solution by the excess of carbonic acid present, when that gas escapes, however—as when the water is allowed to stand exposed to the air, or is boiled—the earthy carbonates fall down as insoluble precipitates, along with the iron which is thrown down as peroxide, or, in the presence of alkaline and earthy carbonates and sulphureted hydrogen, partly as sulphuret of iron.

Buckley and Buehler[3] recognize this reaction and cite it to account for the deposition of pyrite in the Granby area, for hydrogen sulphide will not precipitate iron in acid solutions and organic matter will not reduce ferrous sulphate. Peale and Schweitzer are cited as giving numerous analyses of waters that contain hydrogen sulphide, salts of iron, and carbonic acid. Buckley and Buehler add:

> The presence of this acid [carbonic acid] in excess will cause iron to be carried in solution even in the presence of a large excess of hydrogen sulphide. * * *
>
> In the Granby area it is thought that the presence of carbon dioxide in the oxidized solutions carrying the iron salts was the cause of the retention of the iron. After mingling with the alkaline solutions the iron was precipitated only after the carbonic acid had been largely used in dissolving calcium carbonate.

A. M. Peter[4] also, as a result of his work on the waters of Kentucky, as set forth on pages 94–97, thinks that the zinc, iron, and lead, in alkaline-saline sulphureted waters are held in solution in the presence of hydrogen sulphide by carbon dioxide, being precipitated as sulphides on the escape of carbon dioxide at the surface.

The fact that carbon dioxide (CO_2) or carbonic acid (H_2CO_3) can keep zinc in solution in the presence of hydrogen sulphide can be best understood by taking into account the principle of the "solubility product." The action is like that which occurs in analytical routine when the metals of the copper and arsenic groups are precipitated by hydrogen sulphide from solutions acidified with hydrochloric or sulphuric acids, whereas metals of the zinc group remain in solution. In a mixture of zinc sulphate or other sulphates of the zinc group and hydrogen sulphide the action of these acids in preventing the precipitation of zinc and its related metals depends on the production of a sufficiently high concentration of the hydrogen ion to keep the concentration of the sulphide ion below the point where the solution can become supersaturated with zinc sulphide.[1] Carbonic acid ionizes to a much less extent than the stronger acids, but when it is in excess the concentration of the sulphide ion is smaller than it would be in the same solution without carbon dioxide, and consequently the conditions are such as favor the retention of the zinc in solution.

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[1] Oral communication.

[2] Peter, Robert, Third chemical report: Kentucky Geol. Survey, vol. 3, old ser., p. 246, 1854.

[3] Buckley, E. R., and Buehler, H. A., Geology of the Granby area: Missouri Bur. Geology and Mines, vol. 4, pp. 94–95 [1906].

[4] Personal communication, under date of May 20, 1912.

Carles [2] has shown that barium, as well as strontium and lead, may remain in solution as bicarbonate in the presence of sulphate ions. He writes:

> Researches made by us develop the fact that the waters of Neris-les-Bains contain lead, copper, barium, lithium, fluosilicates, and fluoborates. As these waters are both sulphated and alkaline-bicarbonated, the existence of soluble bicarbonate of barium in the presence of alkaline sulphates has been doubted. This contradiction of Berthollet's laws surprised us at first, for we had supposed that the barium would be precipitated by the sulphate, even in the presence of bicarbonates. Heat and the pressure of carbonic acid seemed to us to tip the balance in favor of the bicarbonates. As we recognized, however, that we have never been able to establish this experimentally, our former doubts persisted.
>
> We recently learned that in the neighborhood of Neris there were several fluorite and even one barite quarry in operation. Analysis shows that the barite contains a sensible proportion of fluosilicates. Its character being established, it occurred to us to submit this barite to the chemico-geologic conditions indicated above, but under a pressure of carbonic gas.
>
> To this end we finely triturated several grams of it and boiled it for three hours in water containing double the quantity of pure carbonate of soda. The solution then contained undecomposed sulphate and fluosilicate of barium, carbonate of soda in excess, and, as the result of their reaction, carbonate of barium, and sulphate and fluosulphate of sodium. A few drops of phenolphthalein indicated the alkalinity of the liquor. It is certain that if we had added to the mixture an acid capable of dissolving the carbonate of barium, the sulphate of soda would have rendered it entirely insoluble.
>
> This mixture suitably diluted with water was put in a siphon for carbonated water and supersaturated with carbonic acid by means of sparklets. At the end of 12 hours the liquid passed through a filter was of irreproachable limpidity.
>
> At this stage it was divided into two equal parts, one of which was introduced into long, narrow tubes and the other was placed in conical Bohemian flasks with very large bases. In this way one of the two liquids had larger air surface and the other had greater depth. The liquids remained thus for several days in the open air without change, but toward the end of the third day the liquid in the flask with the large air surface began to become turbid. In the deep and narrow tubes, on the contrary, turbidity was produced only after about twice the time.
>
> This detail seemed to us important enough to be noted both from the point of view of conservation and of the handling of the bicarbonated waters at the spring.
>
> In order to hasten the decomposition of these two liquids, they were put into a water bath. The carbonic acid is very slowly released, and as a result a very manifest

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[1] Stieglitz, Julius, The elements of qualitative chemical analysis, vol. 1, pp. 199-215, 1912.

[2] Carles, M. P., Présence de la baryte dans les eaux minérales sulphatées: Annales chim. anal., vol. 7, pp. 91-93, 1902.

precipitate is formed. On close examination it was seen that there were two substances of unequal density. In reality analysis discloses first the carbonate of lime, then carbonate of barium, and finally traces of strontium. The barium was in a relatively notable proportion and sufficient to respond clearly to the reactions of the sulphate of lime, sulphate of strontium, chromate of potassium, and finally to be detected by the spectroscope.

Therefore it is indubitable that sulphated and bicarbonated waters with excess of carbonic acid are capable of decomposing sulphate of barium and preserving soluble bicarbonate of barium in the presence of alkaline sulphates.

It is extremely probable that the presence in these same waters of soluble bicarbonate of lead, strontium, and lime is the result of similar reactions.

These facts seem to us to be somewhat important from a hydrologic viewpoint. They prove that we have not yet determined the end of the combinations made by metals in bicarbonated waters.

SOLUBILITY OF LEAD CARBONATE IN WATER CONTAINING CARBON DIOXIDE.

The following data by Leitmeier[1] show that the quantity of lead carbonate soluble in water bears a definite relation to the quantity of carbon dioxide in the water; in other words, in the presence of carbon dioxide, lead carbonate goes into solution as the bicarbonate, the quantity of which in solution is found to be proportional to the concentration of the carbon dioxide.

Lead carbonate is only slightly soluble in water; but it becomes soluble with very small quantities of CO_2, which may be so small that they can not be detected in the usual way, as established by Pleissner and Auerbach, to whom principally we owe our knowledge of the solubility of $PbCO_3$. Therefore the data of W. Böttger and H. Kohlrausch regarding the conductivity and solubility of $PbCO_3$ in pure H_2O are rather uncertain since always small variable quantities of CO_2 were present.

If, as Pleissner and Auerbach[2] have done, we assume a complete ionization of the $PbCO_3$ solution, the solubility product is $L = Pb \times CO_3$, in which Pb represents the concentration of the lead as determined by analysis and CO_3 represents the concentration of carbonic acid. The CO_2 concentration is reckoned according to the formula

$$CO_3'' = \frac{k_2(HCO_3')^2}{k_1(H_2CO_3)}$$

in which k_1 and k_2 are the dissociation constants of carbonic acid. Now if c_0 is the carbonic-acid content of the original solution, then the CO_3'' can be reckoned from the equations

$$HCO_3' = 2Pb^{\cdot\cdot}$$

and

$$c_0 + Pb^{\cdot\cdot} = H_2CO_3 + (HCO_3')$$

From these three equations a fourth may be derived:

$$L \text{ [solubility product]} = \frac{4k_2}{k_1} \frac{(Pb)^{\cdot\cdot 3}}{c_0 - Pb^{\cdot\cdot}}$$

This equation shows the relation of the solubility of lead carbonate to the CO_2 content of the original solution.

The authors give the following table for a temperature of 18° C.:

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[1] Leitmeier, H., Bleicarbonat, in Doelter, C., Handbuch der Mineralchemie, vol. 1, pp. 513–514, 1912.

[2] Pleissner and Auerbach, Über die Löslichkeit einiger Bleiverbindungen, Berlin, 1907; cited by Abegg, R., Handbuch der anorganischen Chemie, Bd. 3, Abt. 2, Leipzig, 1909.

Ratio of solubility of lead carbonate to carbon dioxide content of original solution.

CO_2 content, per liter.		Pb content, per liter.		$L=Pb^{\cdot\cdot}\times CO_3''$.	Corrected CO_2 concentration.	After equation above, with Pb content reckoned on—
Milligrams CO_2.	Millimol c_0.	Milligrams Pb.	Millimol Pb.		Millimol c_0' per liter.	Millimol c_0' per liter.
....	....	....	....	....	0.000	0.0002
0.0	0.000	1.75	0.008	6400×10^{-14}	.011	.008
2.8	.064	6.0	.029	11.9×10^{-14}	.075	.022
5.4	.123	7.0	.034	7.7×10^{-14}	.134	.028
14.4	.328	8.2	.040	3.8×10^{-14}	.339	.039
26.0	.592	9.9	.048	3.5×10^{-14}	.603	.047
43.5	.988	10.9	.053	2.9×10^{-14}	.999	.057
106	2.40	15.7	.076	3.2×10^{-14}	2.41	.076

L [the solubility product] shows a strikingly high figure in solutions containing little CO_2; hence the authors concluded that in these solutions the content of CO_2 was greater than that shown by the analysis. With higher concentration this value does not hold (as may be seen from the table) and the average of the four last determinations may probably be taken as the true figure of the solubility:

$$L=3.3\times10^{-14}$$

From this the solubility of $PbCO_3$ in absolutely CO_2-free water may be reckoned at 0.0002 millimol [or 0.4 milligram] per liter.

SOLUBILITY OF SPHALERITE AND GALENA IN SOLUTIONS IMITATING THE DEEP WATERS.

The original character of the deep waters of the Joplin district having been established by analyses of well waters in Missouri, Kansas, and Oklahoma drawn from the same horizon as those of the Joplin district but impounded beneath the Pennsylvanian shales, it became desirable to ascertain quantitatively the solubility effect upon sphalerite of each of the different constituents of the deep waters and the solubility effect of the combination of these constituents of the natural waters as compared with the effect of distilled water. The deep waters are salt, sulphureted, and carbonated. Common gangue associations of the sulphides are limestone, calcite, and dolomite. To reproduce the conditions of nature as exactly as possible, finely powdered sphalerite intimately mixed with finely powdered calcite was tested for solubility with a dilute solution of sodium chloride, with a saturated solution of hydrogen sulphide, with a saturated solution of carbon dioxide, and finally with a combination of these solutions. The experiments were made in the chemical laboratory of the United States Geological Survey by R. C. Wells, whose discussion of methods used and results obtained is as follows:

A determination of the solubility of sphalerite in water by Weigel[1] gave the value 6.63×10^{-6} mol ZnS per liter at 18° C., equivalent to 0.00043 gram Zn. This value is the solubility calculated from the electric conductivity of a solution of sphalerite obtained by repeatedly washing the sphalerite with "conductivity" water.

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[1] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, pp. 293-300, 1907.

It was desired to determine the solubility of sphalerite in several salt solutions in the presence of calcite. The method of electric conductivity would not be applicable in such a case, so that a direct method was resorted to. This consisted in allowing the solution under investigation to flow very slowly through a tube, 1 centimeter in diameter and 80 centimeters long, filled with powdered sphalerite and calcite, under 40 mesh, and closed with glass wool, which effectually filtered the solution. With a head of about 250 centimeters the flow was about 200 cubic centimeters a day, a rate of flow which was probably sufficiently slow to allow saturation to be attained.

Two preliminary experiments were made without taking special precautions to exclude air from the solutions flowing through the tube. In the first experiment water alone was used, in the second experiment water saturated with carbon dioxide. These two experiments gave, respectively, per liter, with water alone, 0.0003 gram zinc; water with carbon dioxide, 0.0051 gram zinc.

Of course, under these conditions, there may have been some oxidation of the sphalerite. Accordingly in the remaining experiments the solutions were carefully protected from access of air. Boiled water was rapidly cooled, then saturated with the desired gases and preserved in a reservoir whose atmosphere was supplied by a generator of the gas under investigation, or hydrogen. Thus air was practically excluded from all the substances concerned in the experiment. In the four following experiments the solutions passed over the sphalerite and calcite were (1) water containing 1 gram of sodium chloride per liter, (2) water saturated with hydrogen sulphide, (3) water saturated with carbon dioxide, and (4) water containing all these substances. The quantities of zinc found per liter are given below. There is also added an approximate determination of the calcium. The solutions were at a mean temperature of about 23° C. From 1 to 2 liters were used in each experiment and evaporations were conducted in platinum.

Solubility of sphalerite and calcite in certain solutions.

Solution.	Zinc.	Calcium.
	Gram.	*Gram.*
1. Sodium chloride	0.00015	0.015
2. Hydrogen sulphide	.00028	.12
3. Carbon dioxide	.00097	.24
4. All three	.00057	.31

The quantity of zinc found in the dilute solution of salt is less than that found by Weigel in pure water. This discrepancy may be due to the difference in method of determination or, as seems more probable, the calcite may have retained the zinc as basic carbonate. It is not known whether the basic carbonate of zinc is less soluble than sphalerite or not. As for the other determinations, it appears that the presence of hydrogen sulphide increases the solubility of zinc, possibly by forming a hydrosulphide, as well as by carrying the calcium into solution. Carbon dioxide acts similarly, but to a greater extent. A mixture behaves in an intermediate way.

In a separate experiment some boiled water was saturated with carbon dioxide and allowed to stand 5 months, with occasional agitation, in a tightly closed bottle with calcite and sphalerite. The solution then gave on analysis:

	Gram per liter.
Free carbon dioxide	0.374
Calcium	.285
Zinc	.0034

It was desired to determine what effect, if any, dolomite would have upon the solubility of the sphalerite. Experiments similar to those made with a long tube described above were accordingly made, dolomite being used in place of calcite. Three solutions were investigated—(1) water alone, (2) water saturated with carbon dioxide, (3) water saturated with hydrogen sulphide. The solubilities found were as follows, in grams per liter:

Solubility of calcite, dolomite, and sphalerite.

Solution.	Calcium.	Magnesium.	Zinc.
1. Water	0.0059	0.0009	Trace.
2. Carbon dioxide	.130	.051	0.0002
3. Hydrogen sulphide	.294	.070	.00028

These results show about the same order of solubility as the first ones. They have not much quantitative value, as in the first place the quantities of zinc were very small for weighing and in the second place the results would evidently depend somewhat on the length of the tube. It is evident that both carbon dioxide and hydrogen sulphide increase the solubility of sphalerite under the conditions obtaining in the experiments. No doubt the solutions that came through the tube were not saturated with the gases even if they started in that condition, so that the equilibrium reached must have been one somewhat between that corresponding either to an excess of calcite or an excess of the gases. The fractional removal of the calcium from the magnesium is also indicated in the last experiments.

In order to obtain greater accuracy another set of experiments was undertaken by Wells, in which he used much larger quantities of solution, so that the quantities of zinc obtained in solution should, when precipitated, be easily weighable. In a duplicate set of experiments galena was substituted for sphalerite to determine the relative solubilities of the two minerals under the different conditions of the experiments. The results are discussed by Wells as follows:

The term "solubility" is used with various meanings, two of which it may be well to distinguish before the experiments that follow are described. In a rather loose sense, sphalerite and galena may be said to be soluble in atmospheric water under ordinary conditions at the surface of the earth; but actually before appreciable solution can be effected under these conditions the sulphides are oxidized and the compounds that go into solution are likely to be the very soluble sulphate of zinc and the sulphate of lead. In other words, the solution is effected through a radical chemical change in the initial substance, and this substance can not again be obtained in solid form by mere concentration of the solution. In a stricter sense a substance is soluble in a given solvent when its constituents are present in the solution in such form that the original substance may be obtained again in the solid form by concentration. It is this kind of solubility that was in mind in the following experiments.

Let us consider first the solubility of sphalerite. In accordance with the conception of the solubility product a solution of sphalerite may hold a zinc content varying anywhere from practically nothing up to perhaps a gram of zinc per liter, the quantity depending on a similar inverse variation in sulphide content. The sulphide ion content in turn depends on both the total sulphide content and the acidity of the solution. In the following experiments it was sought to imitate natural conditions by fixing the acidity of the solution by an excess of dolomitic limestone; that is, the acidity could not exceed if it could equal that of a solution saturated with carbon dioxide or hydrogen sulphide. The Ca:Mg ratio of this dolomite was 1:0.73.

Experiment 1. Eighteen liters of distilled water were agitated in a large carboy for several days with a little powdered iron for the purpose of removing all oxygen. About 20 grams of sodium chloride (to prevent colloidal effects) and 10 grams of powdered sphalerite were then added. The carboy was sealed, rotated for half a day, and then allowed to stand a week. After filtering, the solution appeared neutral to phenolphthalein but somewhat alkaline to methyl orange; that is, it was practically neutral. Evaporated, 17.6 liters gave 0.39 gram FeO, 0.39 gram CaO, 0.0008 gram MnO, and 0.0006 gram ZnO. This is 0.000027 gram Zn per liter, a value which represents, in my opinion, a maximum for the zinc content of a solution of sphalerite in practically neutral water.

Experiment 2. Eighteen liters of water were saturated with hydrogen sulphide. Twenty grams of sodium chloride, 50 grams of dolomite, and 10 grams of sphalerite were added, and the introduction of hydrogen sulphide continued for several days. After rotation and standing as in the previous experiment the solution was found to contain 1.03 grams H_2S and 0.000019 gram Zn per liter. Briefly, the quantity of zinc was not appreciably different in the solution containing hydrogen sulphide from that obtained in the first experiment.

Experiment 3. In this experiment no special precautions were taken to free the water entirely from oxygen; in consequence some zinc sulphate may have been formed by oxidation of the sphalerite. It was expected that, if formed, this would react with the dolomite to produce a basic carbonate of zinc. The experiment was really therefore a determination of the solubility of the basic carbonate of zinc. Eighteen liters of water were taken, 20 grams of sodium chloride, 15 grams of dolomite, and 10 grams of sphalerite. By the same process employed in the other experiments the solution finally gave 0.00008 gram Zn per liter, a value very nearly of the same order as the solubility of zinc sulphide in water.

Experiment 4. The conditions were similar to those last described except for the introduction of carbon dioxide in excess. As before, it was expected that if much zinc sulphate were present it would give zinc carbonate as the solid phase and zinc bicarbonate in solution. The products obtained from 15.6 liters were 15.6 grams CO_2 (existing as 10.6 grams free CO_2 and 5.0 grams bicarbonate radicle), 1.95 grams CaO, 1.29 grams MgO, 0.0661 gram $ZnSO_4$. This is 0.0017 gram Zn per liter. The increased content of zinc due to the carbon dioxide, 0.0017 compared with 0.00008, is clearly shown. The part played by the sphalerite in this experiment may have been to furnish some zinc sulphate through oxidation or in addition it may have reacted with the carbon dioxide to form some zinc bicarbonate and hydrogen sulphide.

Experiments 5, 6, 7, and 8. Experiments exactly similar to these above were made, galena being used in place of sphalerite. The quantity of lead found in every experiment was too small to admit of analytical determination, although hydrogen sulphide produced a cloud in all the concentrates, that produced in the solution which had contained an excess of carbon dioxide being distinctly heavier than the others. Presumably these faint precipitates were due wholly to lead, but this presumption could not be positively established. It is evident that galena is appreciably less soluble than sphalerite—so insoluble, in fact, that 18 liters of a neutral solution do not contain as much as 0.1 milligram of lead. Knox [1] has given for the solubility product of lead sulphide the value 2.6×10^{-15}; but Stieglitz [2] has pointed out that the true value is probably much smaller than this. The solubility relations of lead carbonate in the presence of an excess of carbon dioxide have been more completely studied by Pleissner and Auerbach, whose results leave nothing to be desired. (See pp. 56–57.)

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[1] Knox, Joseph, A study of the sulphur anion and of complex sulphur anions: Faraday Soc. Trans., vol. 4, p. 44, 1908.

[2] Stieglitz, Julius, The elements of qualitative analysis, pt. 1, p. 212, 1911.

PRECIPITATION AS SULPHIDES.

PRECIPITATION BY HYDROGEN SULPHIDE.

Among the suggested precipitants of the sulphides which may be regarded as having been efficient in the Joplin region are hydrogen sulphide, thiosulphates, and organic matter. The most effective of these is undoubtedly hydrogen sulphide, which is present in greater or less quantity in practically all the deep waters of the region. It is released in the formation of carbonates and bicarbonates of the metals by the action of carbonic acid (H_2CO_3) upon the sulphides of the metals, as shown in the reactions indicated in the foregoing pages. It is freed also in the formation of calcium and sodium zincates and sulphozincates by the action of sodium and calcium carbonates and bicarbonates upon zinc sulphide. It is therefore a by-product of the solution of the disseminated sulphides according to those reactions which are believed to have been the most efficient in the segregation of the ore deposits. Hydrogen sulphide may also, to some extent, have been liberated by the hydrolytic action of the ground water on pyrite, as indicated in experiments made by Clark.[1]

By these reactions hydrogen sulphide is liberated in equivalents of the metals taken into solution and is carried along in the solution of the metals by the artesian flow of the underground circulation until it reaches the surface, where the carbon dioxide escapes and the hydrogen sulphide precipitates the metals as sulphides.

A fact which has an important bearing on the concentration of the carbon dioxide in solution in the underground water and on the quantity which may escape at the surface is that meteoric waters entering the artesian circulation upon the crest of the Ozark uplift carry dissolved oxygen. This will react with the iron pyrites disseminated through the rocks, liberating sulphuric acid according to this equation:

$$FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$$

The free sulphuric acid attacks the limestones through which the water circulates, resulting in the formation of calcium sulphate and carbon dioxide, thus:

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$$

In their journey downward and outward through the Cambrian and Ordovician limestones the waters thus become more and more acid through the liberation of carbon dioxide, the concentration of which rises higher and higher with increase in depth. The carbon dioxide liberated in the deep underground water, which is under hydrostatic pressure, goes into solution in that water in much greater volume than in water at surface pressure. When the waters finally rise to the surface, the pressure of the carbon dioxide is lowered and it escapes into the atmosphere. The acidity of the water is thereby decreased and the hydrogen sulphide present becomes able to precipitate the metals as sulphides, the reverse of the action described on pages 54–55 in the discussion of the solution of zinc sulphide as bicarbonate in the presence of carbon dioxide in excess.

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[1] Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., vol. 1, p. 115, 1914.

PRECIPITATION BY THIOSULPHATES.

Stokes[1] has shown that pyrite and marcasite are decomposed by circulating alkaline waters with the formation of alkali sulphides and thiosulphates. Allen[2] and associates precipitated zinc sulphide from sulphate solution by the action of sodium thiosulphate at a temperature of 100° C. Thiosulphate radicle was found by Wells in the water from the Church mine and by Failyer and Willard in water from the well at Columbus, Kans. (Analyses Nos. 18 and 5 in synoptical table, p. 149). It was also recognized by Hillebrand in water from the Federal Loan mine (No. 81 in the table) and from the Black Prince mines, in California. It was found by Headden in the Doughty Black Spring (No. 6 in the table) in Colorado, and by Waring in the Johnson well (No. 106 in the table) in Texas. Thiosulphate is seldom tested for in commercial analyses, and is undoubtedly more common in the deep waters of the Joplin region than the analyses indicate. It therefore may have contributed to the precipitation of the sulphide ore bodies of the region by reactions analogous to the following, cited by Allen:

$$ZnSO_4 + 4Na_2S_2O_3 = ZnS + 4Na_2SO_4 + 4S$$

The free sulphur that gives the milky bluish color to the deep-well waters stored in the reservoirs may be due in part to sulphur set free in the foregoing reaction as well as to sulphur freed by the oxidation of hydrogen sulphide, thus:

$$H_2S + O = H_2O + S$$

PRECIPITATION BY ORGANIC MATTER.

The reduction of sulphates by organic matter, though generally accepted as a fact, does not seem to have been actually demonstrated by any experiment yet reported that negatives the possibility of the evolution of hydrogen sulphide from organic matter by the agency of bacteria or even the possibility of the direct reduction of sulphates by sulphur bacteria. The writer has been orally informed by Dr. E. T. Allen, of the Geophysical Laboratory of the Carnegie Institution, by Prof. H. A. Buehler, of the Missouri Geological Survey, and by Dr. Chase Palmer, of the United States Geological Survey, that they have not succeeded in reducing sulphates by organic matter. Clark[1] put cupric sulphate, ferrous sulphate, sulphur dioxide, and powdered coal in a flask, which was shaken daily for 122 days, but there was no formation of copper sulphide at the end of the experiment, from which he concludes that carbon alone would not precipitate the sulphide. Hoppe-Seyler[2] describes the reduction of a sulphate by nascent methane (CH_4) derived from the fermentation of cellulose, but the fermentation was probably caused by bacteria, and hydrogen sulphide may have been thus evolved in and have caused the reduction of the sulphate. Hydrogen sulphide is plentiful in certain Russian lakes and seas, cited by Stutzer,[3] which do not have an effective vertical circulation. In the water of Wiessowo Salt Lake, for instance, there is 30 times as much hydrogen sulphide at a depth of 61.3 feet as at a depth of 52 feet. In the Black Sea there is about 20 times as much hydrogen sulphide at a depth of 8,000 feet as at a depth of 700 feet. This hydrogen sulphide results from the reduction of sulphates in the sea water by products of the decomposition of organic substances on the sea floor, through the action of anaerobic bacteria. According to Murray and Irvine[4] this decomposition takes place in two stages, represented by these reactions:

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[1] Stokes, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, pp. 14–15, 1907.

[2] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: Am. Jour. Sci., 4th ser., vol. 34, pp. 351, 352, 1912.

$$MgSO_4 + 2C = 2CO_2 + MgS$$
$$MgS + CO_2 + H_2O = MgCO_3 + H_2S$$

No laboratory proof is given that the sulphate is actually reduced by the organic matter as indicated in the first reaction. It may be noted in passing that although ferrous sulphide is of common occurrence in deep-sea sediments, iron disulphide has been recognized from such deposits in the Black Sea alone, where it occurs as minute rods of pyrite [marcasite?].

Allen, Crenshaw, and Johnson[5] have shown that ferrous sulphate can not be reduced to the disulphide by the action of organic matter, though they find that hydrogen sulphide will reduce ferric sulphate to the disulphide in two stages as follows:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S$$
$$FeSO_4 + S + H_2S = FeS_2 + H_2SO_4$$

In oxidized solutions some of the ferrous sulphate will be oxidized to ferric sulphate, thus:

$$6FeSO_4 + 3O = 2Fe_2(SO_4)_3 + Fe_2O_3$$

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[1] Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., vol. 1, No. 2, p. 117, 1914.

[2] Zeitschr. physiolog. Chemie, Band 10, p. 401, 1886, cited from Stutzer, O., Die wichtigsten Lagerstätten der "Nicht-Erze," p. 258, 1911.

[3] Stutzer, O., Die wichtigsten Lagerstätten der "Nicht-Erze," p. 260, 1911.

[4] Murray, John, and Irvine, Robert, Roy. Soc. Edinburgh Trans., vol. 37, p. 496, 1895.

[5] Allen, E. T., Crenshaw, J. L., and Johnson, John, The mineral sulphides of iron, with crystallographic study by E. S. Larsen: Am. Jour. Sci., 4th ser., vol. 33, pp. 171-173, 1912.

Any natural water containing iron sulphate will contain also sulphates of the alkaline earths and perhaps also sulphates of the alkalies. Schweitzer[1] quotes T. Sterry Hunt[2] as authority for the statement that when water containing calcium sulphate and carbon dioxide comes into contact with organic matter hydrogen sulphide is formed, thus:

$$CaSO_4 + CH_4 = CaS + CO_2 + H_2O$$
$$CaS + CO_2 + H_2O = CaCO_3 + H_2S$$

Schweitzer says:

> This action is so well established that in bottling waters containing much carbonic acid and calcium sulphate great care must be exercised not to let fibers of straw or similar organic matter get into the bottles, since in such case sulphureted hydrogen would be sure to make its appearance.

Bischof[3] also notes the decomposition of alkaline and earthy sulphates by carbonaceous substances, with the formation of sulphides and hydrogen sulphide, especially in mineral waters which have remained in corked bottles for some time. He hermetically sealed several bottles of mineral waters, containing a notable quantity of sulphate of soda as well as iron in solution, to which he had added a small quantity of sugar. After standing three and one-half years there was complete reduction of the sulphate of soda, with the evolution of hydrogen sulphide and deposition of a flocculent black powder which, as shown by analyses, "had nearly the composition of iron pyrites."

Stutzer[4] uses reactions similar to the foregoing to account for the hydrogen sulphide which by oxidation has formed native sulphur deposits.

Therefore, whether or not the sulphates of the metals are reducible by organic matter, when the solutions containing sulphates come into contact with shales rich in decomposable organic matter there will be formed hydrogen sulphide, concerning the ability of which to precipitate the metallic sulphides there is no question.

The fact that charcoal reduces gold cyanide solution and precipitates metallic gold has long been known. Clennell[5] says:

> No satisfactory explanation of the reaction has yet been given. It has been alleged to be due to occluded hydrogen, or hydrocarbons contained in the pores of the charcoal. The method has been used in several small plants in Victoria, Australia, on a working scale.

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[1] Schweitzer, Paul, The mineral waters of Missouri: Missouri Geol. Survey, vol. 3, pp. 4, 10, 1892.

[2] Hunt, T. Sterry, Chemical and geological essays, 2d ed., pp. 99, 230, 1878.

[3] Bischof, Gustav, Elements of chemical and physical geology (translated by B. H. Paul and Dr. J. Drummond), vol. 1, pp. 15, 163, London, Cavendish Society, 1854.

[4] Stutzer, O., Die wichtigsten Lagerstätten der "Nicht-Erze," p. 258, 1911.

[5] Clennell, J. E., The cyanide handbook, p. 308, New York, 1910.

Recent work by Green[1] indicates that the occluded gas chiefly effective in the reduction is carbon monoxide, with a minor quantity of hydrogen. It seems not unreasonable to conclude that the precipitating action of carbonaceous shales on the ore solutions may be due in part to such occluded gases. Shales rich in carbonaceous matter are laid down under conditions unfavorable to complete oxidation, and the gases mentioned may be among those formed and adsorbed by the shale.

As has been pointed out in the preceding pages, the sulphate is not the only form in which the sulphide of a metal is taken into solution and transported; in fact in the deeper circulation and in the ascending currents soluble forms like the bicarbonates, the zincates, and the double sulphides are believed to be relatively much more effective than the sulphates in removing the disseminated sulphides and transporting them to the surface. As deposits of the metallic sulphides are common in the Joplin district in such relation to bodies of shale as to indicate that they were deposited from ascending solutions and were precipitated through influence of the shale, it becomes important to inquire how the organic matter of the shale may cause precipitation of sulphides. The reducing power of organic matter has, of course, been recognized and reactions have been written[2] which involve the carbonates of the metals, the sulphates of the alkaline earths, and the carbon of organic matter, and indicate the precipitation of metallic sulphides, thus:

$$ZnCO_3 + CaSO_4 + 2H_2O + 2C = ZnS + CaCO_3 + 2H_2CO_3$$

The changes involved in this reaction take place in three stages, thus:

$$\begin{aligned} &CaSO_4 + 2C = CaS + 2CO_2 \\ &CaS + CO_2 + H_2O = CaCO_3 + H_2S \\ &ZnCO_3 + H_2S = ZnS + H_2CO_3 \end{aligned}$$

It is therefore essentially a reduction of calcium sulphate by organic matter to obtain hydrogen sulphide for a precipitant of the zinc, with carbon dioxide as a by-product of the reaction. As has been pointed out, an excess of carbon dioxide will hold zinc in solution in the presence of hydrogen sulphide. Since the lead and zinc bearing deep waters of the district, as shown by the analyses given on pages 124–140, are already carbonated and sulphureted, it is not probable that the sulphides will be precipitated from the deeper waters of the district by the foregoing reaction.

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[1] Green, Morris, The effect of charcoal in gold-bearing cyanide solutions with reference to the precipitation of gold: Inst. Min. and Met. Trans., vol. 23, p. 77, 1914.

[2] Jenney, W. P., The chemistry of ore deposition: Am. Inst. Min. Eng. Trans., vol. 33, p. 450, 1903.

If, however, the reducing power of the organic matter be considered as applying directly to the zinc carbonate, the following reaction is very probably obtained, CH_4 being used as a representative hydrocarbon:

$$2ZnCO_3+2H_2S+2C=2ZnS+CH_4+3CO_2$$

or with the bicarbonate thus:

$$2Zn(HCO_3)_2+2H_2S+3C=2ZnS+CH_4+2H_2O+6CO_2$$

and with the zincate thus:

$$CaZnO_2+2H_2S+2C=ZnS+CaS+CH_4+CO_2$$

In case the zinc be carried as the sulphozincate, it does not appear that the organic matter of the shale will have any influence on the splitting up of the complex sulphide, that only happening when the excess of hydrogen sulphide and carbon dioxide escape at the surface.

SUMMARY OF CHEMISTRY OF LEAD AND ZINC SOLUTIONS.

It has been shown that the metals disseminated as sulphides may be taken into solution and transported as sulphates, as chlorides, as sulphides and hydrosulphides, as zincates and sulphozincates, and as carbonates and bicarbonates. Anticipating a little, it may be stated at this point that the writer, while recognizing all these as possible forms of transportation, each of which has doubtless been effective at times, nevertheless believes that the great mass of the ores has been transported as bicarbonates. He conceives that the metals, which were disseminated as sulphides through the limestones and dolomites, were taken into solution as bicarbonates by the alkaline-saline water containing dissolved carbon dioxide, according to reactions like the following:

$$ZnS+2CO_2+2H_2O=Zn(HCO_3)_2+H_2S$$

This solution, incorporated into the artesian circulation, eventually rose to the surface, where the carbon dioxide escaped and the metals were again precipitated as sulphides by the equivalent of hydrogen sulphide resulting from their solution as bicarbonates and still remaining in the circulation. If the metals were in part carried in solution as double sulphides they, too, would be deposited on the escape of the hydrogen sulphide at the surface, or on its being used up in the precipitation of the metals in solution as bicarbonates.

SOURCE OF THE METALS.

METALS IN IGNEOUS ROCKS.

RESULTS OF CHEMICAL ANALYSES.

Winslow[1] has adequately summarized the earlier investigations bearing on the occurrence of lead and zinc in igneous rocks, in sediments (both shales and limestones), and in sea water. In brief, lead and zinc are found commonly in minute quantities in all these. Clarke and Steiger[1] give the lead and zinc content of a composite made up of 329 samples of igneous rocks which have been analyzed in the United States Geological Survey's chemical laboratory, as follows:

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[1] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 6, pp. 30-33, 1894.

Lead and zinc content of a composite sample of igneous rocks.

[George Steiger, analyst.]

Nickel (Ni)	0.00515
Arsenic (As)	.00048
Copper (Cu)	.00932
Lead (Pb)	.00075
Zinc (Zn)	.00513

Clarke and Steiger[1] say:

> In a series of 36 igneous and metamorphic rocks of British Guiana, Harrison found a mean percentage of 0.025 copper. In 23 of his samples lead was also sought for, and detected in 5 of them, the maximum amount being 0.02 per cent. In a typical specimen of the Columbia River basalt Wells found 0.034 of copper, and the same quantity was determined by Jensen in an andesite from Fiji. In the porphyries of Leadville, Colo., Hillebrand was able to determine lead. Out of 18 samples, taken at points remote from ore bodies, the average amount found was 0.002 per cent of PbO. One porphyry also yielded 0.008 per cent of zinc oxide, and a rhyolite contained 0.0043 per cent.

Winslow[2] gives the results of the determination in duplicate of copper, lead, and zinc in four igneous rocks from southeastern Missouri by J. D. Robertson, using large quantities of material. These figures are given in detail on page 78.

Finlayson[3] gives the following determinations of the lead and zinc content of a number of both igneous and sedimentary rocks of Great Britain. The large-quantity methods of Hillebrand and of Robertson were used.

Lead and zinc content of igneous and sedimentary rocks from Great Britain.

	Locality.	Lead.	Zinc.
Igneous rocks:			
Granite	Foxdale	0.004	0.005
Do	Threlkeld	.003	.011
Do	Glendalough	.004	.001
Do	Dartmoor	.002	.002
Diabase (Whin Sill)	Rotherhope	.003	.0005
Diabase (Toadstone)	Darleydale	.001	.001
Volcanic ash	Conway	.0025	.000
Do	Greenside	.006	.002
Total		.0255	.0125
Average		.0032	.0016
Sedimentary rocks:			
Slate	Leadhills	.001	.000
Limestone	Halkyn	.0005	.0015
Do	Matlock	.001	.0005
Do	Alston	.0015	.001
Total		.004	.003
Average		.001	.00075

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[1] Clarke, F. W., and Steiger, George, The relative abundance of several metallic elements: Washington Acad. Sci. Jour., vol. 4, p. 60, 1914.

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, p. 479, 1894.

[3] Finlayson, A. M., Problems of ore deposition in the lead and zinc veins of Great Britain: Geol. Soc. London Quart. Jour., vol. 66, p. 301, 1910.

Finlayson[1] says:

> The foregoing analyses, like those of Luther Wagoner for gold and silver in rock at San Francisco,[2] show a higher percentage of metals in the igneous than in the sedimentary rocks, suggesting the conclusion that the metals in the later rocks have been derived by denudation from the older igneous and crystalline rocks.

That the igneous rocks are the ultimate source of the metals in general, including those disseminated through the limestones, will be generally admitted.

SOLUTION OF THE METALS FROM THE CRYSTALLINE ROCKS AND THEIR TRANSPORTATION TO THE SEA.

The metals are included in the igneous rocks probably in part as small disseminated particles of the sulphides and probably in part as integral constituents of the minerals, chiefly silicates, which make up the rocks. The metals are freed from their environment mainly by the decomposition and erosion of the rocks, the sulphides of the metals being oxidized to the sulphates, which are easily soluble in the ground waters, and the silicates of the metals being decomposed and taken into solution, principally as bicarbonates. The metals in the rocks below the immediate surficial zone may be in part taken into solution by the ground water circulating in deeper joints and crevices of the rocks, being transported chiefly as bicarbonates.

The transfer of the metals by streams as sulphates may be indicated by the significant observations of Dr. E. H. S. Bailey[3] on the comparative zinc and sulphate content of the water of Spring River in Missouri and Kansas at different stations above, in, and below the Joplin zinc and lead fields.

The essential parts of the analyses made by Bailey are included in the following table:

Partial analyses of water of Spring River at places in Missouri and Kansas.

[In parts per million. E. H. S. Bailey, analyst.]

Station and date.	Calcium.	Sulphate radicle (SO_4).	Zinc.	Total solids.
1. Carthage, Mo., Mar. 7, 1904	50.0	25.0	Undet.	178.0
2. Badger, Kans., Mar. 31, 1905	52.6	70.0	16.2	279.6
3. Above dam at Lowell, Kans., Mar. 30, 1905	42.2	157.2	3.7	228.0
4. Below dam at Lowell, Kans., Mar. 30, 1905	40.4	19.0	10.0	179.0
5. Baxter Springs, Kans., Apr. 5–15, 1907	68.0	72.0	Undet.	250.0

Between stations 2 and 3 Shawnee Creek empties into Spring River from the northwest, draining an agricultural country. Between stations 3 and 4 Shoal Creek enters from the east, carrying 67.2 parts calcium per million, 15.6 parts sulphate radicle (SO_4), 11 parts zinc, and 198.8 parts total solids. The influence of the stretch of quiet water above the Lowell dam, between stations 2 and 4, on the total solids is recognizable, for they decrease through that stretch. As a whole, the results are less convincing than they would be had the samples been taken consecutively downstream so as to insure nearly similar conditions for sampling. Determinations of zinc at stations 1 and 5 would have added to the value of the data.

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[1] Finlayson, A. M., op. cit.

[2] Wagoner, Luther, The detection and estimation of small quantities of gold and silver: Am. Inst. Min. Eng. Trans., vol. 31, pp. 809–810, 1901.

[3] Bailey, E. H. S., Preliminary report on stream pollution by mine waters in southeastern Kansas: U. S. Geol. Survey Water-Supply Paper 273, pp. 349–361, 1911.

Bailey says:[1]

> Since the zinc seems to diminish in quantity, the question arises whether this diminution is due merely to dilution with waters of other streams or to precipitation by calcium and magnesium carbonates in solution in the water. As there still remains in the water at Lowell more SO_4 than is found in the water in the upper part of the course of the stream, it would seem to indicate that much of the zinc had been precipitated, otherwise it would have increased proportionately with the sulphates.

Bailey concludes that the zinc has been precipitated as the carbonate by reaction with the calcium and magnesium bicarbonate in solution in the water thus:

$$ZnSO_4 + Ca(H_2CO_3)_2 = ZnCO_3 + CaSO_4 + H_2O + CO_2$$

Apparently the metal may take any one of four possible courses when zinc sulphate is added to stream water containing calcium bicarbonate in solution. It may continue in solution as the sulphate; it may be precipitated as the carbonate according to the foregoing reaction; it may react with the calcium bicarbonate and remain in solution as zinc bicarbonate; or it may be reduced from the sulphate and precipitated as the sulphide by hydrogen sulphide in the stream. The very small quantity of sulphate radicle (SO_4) at station 4, below the Lowell dam, seems to indicate that the reducing reaction last mentioned is notably effective in the stagnant water above the dam. Such zinc bicarbonate as is formed will remain in solution unless the solution encounters hydrogen sulphide, in which case the zinc will be precipitated as the sulphide.

DEPOSITION OF DISSEMINATED METALS IN OCEANIC SEDIMENTS.

Deposition in clays and calcareous muds.—As the nature of sediments is determined by conditions in the drainage basin furnishing them, a sea in which carbonaceous shale and coal are being deposited will be bordered by low-lying land and will be fed by streams laden with carbonaceous sediment. Zinc taken into solution as the sulphate from the oxidation of the sulphides and carried seaward by such streams stands the various chances of precipitation outlined above. Taken into solution and carried as the bicarbonate it may be precipitated by lowering the concentration of carbonate radicle (CO_3) in the water (not a probable contingency in such water) or by hydrogen sulphide, the supply of which, owing to the paucity of animal life in such waters and to their prevention of decay, is likely to be small. The zinc bicarbonate in solution which is not precipitated either in the streams on the way to the sea or in the coal-depositing sea itself will be diffused through the sea until it reaches beyond the limits of deposition of the coal measures, where animal life and sulphur bacteria are abundant and hydrogen sulphide is available for the precipitation of the metal as sulphide, and it will thus be deposited in calcareous sediments. Hence zinc sulphate solutions stand many chances of deposition before reaching the sea, whereas zinc bicarbonate solutions will likely pass beyond the coal-measure sea and be deposited where limestones are being laid down.

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[1] Bailey, E. H. S., op. cit., p. 354.

Streams contributing to a sea where limestones are being laid down adjacent to land will carry lime, magnesium, and carbonate radicle (CO_3) in excess, but will carry little carbonaceous matter. Much of the mineral matter carried by the stream will be taken into solution by the underground drainage and will be contributed to the surface streams by springs. Under these circumstances zinc and lead disseminated through the rocks as sulphides will be taken into solution as bicarbonates, as shown by Wells's experiments, described on a previous page, and will be carried out to sea, where precipitation as sulphide by the hydrogen sulphide always present in sea water will be a natural consequence.

Reasoning a priori we should conclude that among the sedimentary rocks the natural places of deposition of primary disseminations of lead and zinc are the limestones, and that the occurrence of such deposits should be less common among the carbonaceous sediments. Peter has pointed out (see p. 95) that the waters which carry zinc in Kentucky are principally those derived from the limestone formations of the Ordovician system. It is true that analyses show the presence of lead and zinc in carbonaceous sediments, as is indicated above and as has been shown for various shale formations of Europe by Dieulefait, Bischof, and Sandberger. But disseminated lead and zinc in carbonaceous sediments that overlie limestones which contain lead and zinc and which are saturated by water under artesian pressure can not be safely assumed to be of primary or sedigenetic origin, for the conditions indicated afford every facility for the precipitation of the metals of ascending solutions in the shale.

Deposition in dolomitic muds.—It will be noted that the Cambrian and Ordovician limestones of the Ozark region, taken in this report to be the immediate source of the metals, are dolomitic. The Galena dolomite, according to Chamberlin, Van Hise, Bain, Grant, and others, originally held in disseminated form the lead and zinc which was later concentrated into the ore deposits of the upper Mississippi Valley region. The zinc deposits of the Arbuckle Mountains, Okla., are found in the dolomitic Arbuckle limestone. The east Tennessee deposits occur in the Knox dolomite and are believed by Purdue to have been derived from that formation. The Virginia deposits are likewise believed by Watson to have been derived from disseminated lead and zinc in the dolomitic Shenandoah limestone. The Ueberroth, Saucon, and Hartman zinc mines of Pennsylvania occur in magnesian limestone. So, too, many of the other deposits, which are later mentioned as occurring in the central valley of the United States are found in dolomitic limestone and are believed to have been segregated from a minutely disseminated state in such limestones. Indeed, the association of ore deposits with dolomitic limestones has long been noted, and T. Sterry Hunt[1] has offered this suggestion to explain the association:

> In the preceding sections we have supposed the waters mingling with the solution of sulphate of magnesia to contain no other bicarbonate than that of lime; but bicarbonate of soda is often present in large proportion in natural waters, and the addition of this salt to sea water or other solutions containing chlorides and sulphates of lime and magnesia will, as we have shown, separate the lime as carbonate and give rise to liquids, which, without being concentrated brines, as in the previous case, will contain sulphate of magnesia, but no lime salts. A further portion of bicarbonate of soda will produce bicarbonate of magnesia, by the evaporation of whose solutions, as before, hydrated carbonate of magnesia would be deposited, mingled with the carbonate of lime which accompanies the alkaline salt and, in the case of the waters of alkaline springs, with the compounds of iron, manganese, zinc, nickel, lead, copper, arsenic, chrome, and other metals which springs of this kind still bring to the surface. In this way the metalliferous character of many dolomites is explained.

METALS DISSEMINATED IN OCEANIC SEDIMENTS.

There are several good analyses of deep-sea sediments that show their lead and zinc content. These consist of the analysis of manganese nodules collected by the *Challenger*[2] expedition, and the analyses made in the chemical laboratory of the United States Geological Survey of composite samples of pelagic "red clay" and terrigenous "blue mud" collected by the *Challenger* expedition and reported by Clarke.[3] To these should be added the analyses, cited by Clarke and Steiger,[4] of a composite sample of silt from the Mississippi River delta. The analyses of the oceanic sediments which follow differ in their form of statement from those given by Clarke in that they present all the constituents found by the analysts, whereas Clarke rejected calcium carbonate, sea salts, etc., and recalculated to 100 per cent.

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[1] Chemical and geological essays, 2d ed., p. 88, 1878.

[2] Gibson, John, Report on an analytical examination of manganese nodules; Deep-sea deposits: Voyage of H. M. S. *Challenger*, Appendix 2, p. 422, 1891.

[3] Clarke, F. W., The data of geochemistry, 2d ed.: U. S. Geol. Survey Bull. 491, p. 490, 1911.

[4] Clarke, F. W., and Steiger, George, The relative abundance of several metallic elements: Washington Acad. Sci. Jour., vol. 4, p. 59, 1914.

Analyses of deep-sea and delta deposits.

	1	2	3	4
SiO_2	45.32	13.38	46.64	69.96
Al_2O_3	13.26	5.49	14.08	10.52
Fe_2O_3	7.20	14.33	4.14	3.47
FeO	.70	....	1.88	
MgO	3.05	2.34	1.95	1.41
CaO	6.82	2.31	7.20	2.17
Na_2O	3.63	1.81	2.98	1.51
K_2O	2.43	.25	1.84	2.30
H_2O-	3.28	23.00	4.73	3.78
H_2O+	5.93	6.65	5.86	1.96
TiO_2	.82	.13	1.84	.59
ZrO_2	(?)	....	None.	.05
CO_2	3.91	.29	4.05	1.40
P_2O_5	.25	.13	.17	.18
SO_3	.48	.83	.32	.03
Cl	2.77	.96	2.25	.30
F	None.	Trace.	....	.07
S	Trace?	....	.11	.07
Te	....	Trace.	....	....
BaO	1.70	.12	.05	.08
SrO	.046	.02	.025	Trace.
Li_2O	None.	Trace.	....	....
$(NH_4)_2O$	....	.02	....	....
MnO	.83	21.46	.10	.06
V_2O_3	.035	.07	.028	.02
Cr_2O_3	.011	....	.044	.01
MoO_3	Trace.	.10	None.	....
As_2O_3	.0007	None.	Trace.	.0004
(Ni, Co)O	.032	1.26	.080	.017
CuO	.020	.37	.009	.0043
PbO	.007	.05	.0004	.0002
ZnO	.004	.10	.0087	.001
Tl_2O	....	.03	....	....
C	....	....	1.38	.66
O	....	4.71	....	....
	101.01	100.21	101.775	100.6229
Less O	.62	.22	.56	.12
	100.39	99.99	101.215	100.5029

1. Pelagic red clay; composite of 51 samples. George Steiger, analyst.
2. Manganese nodule; from depth of 2,375 fathoms. John Gibson, analyst.
3. Terrigenous blue mud; composite of 52 samples. George Steiger, analyst.
4. Mississippi delta mud; composite of 235 samples. George Steiger, analyst.

The analyses just given show that definitely measurable quantities of lead and zinc occur in both the terrigenous and the pelagic deposits of the ocean. As each of the analyses of the oceanic sediment represents a composite of over 50 samples, taken from widely separated places, they may be safely used to obtain some notion of the total quantity of these metals in the deep-sea sediments. According to the *Challenger* reports, the area of terrigenous "blue mud" is 14,500,000 square miles and the area of the pelagic "red clay" is 51,500,000 square miles. Seelheim's experiments on the porosity of the sediment from an emulsion of fine clay and water are summarized by King[1] as follows:

> Seelheim[2] has shown that when an emulsion of fine clay and water is allowed to stand quietly for some time under conditions where no jarring can take place the clay subsides, assuming a stratified condition, but containing a large amount of water.

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[1] King, F. H., Principles and conditions of the movements of ground water: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, p. 78, 1899.

[2] Seelheim, F., Methoden zur Bestimmung der Durchlässigkeit des Bodens: Zeitschr. anal. Chemie, vol. 19, p. 387, 1880.

He found where no jarring took place that the upper layers contained more water than the lower ones, the proportion being 1 volume of clay to 3.84 volumes of water in the upper strata and 1 volume of clay to 1.78 volumes of water in the lower strata. That is to say, in the loosest settling 79.34 per cent of the volume of the sediment was water and in the closer packing there was still 64.03 per cent of pore space.

Where the settling was allowed to take place under frequent jarrings Seelheim secured a uniform texture throughout and greater compactness, but there was still a pore space of 54.54 per cent. He further showed that there was no sensible reduction of pore space when the sedimentation was caused to take place under a pressure of 102 feet of water instead of a few feet. Further than this, there is no reason to suppose that the pore space of sediments laid down under water will not be filled very largely with the water in which they are deposited.

It will apparently be safe, therefore, to assume an average porosity of 50 per cent for sediments like the red clay and the blue mud; and this assumption has practically been made by Stabler,[1] who takes 85 pounds as the average weight of a cubic foot of reservoir sediment, whereas if these sediments are compacted under high pressure into the form of rock matter they weigh 165 pounds to the cubic foot. Though 85 pounds is undoubtedly too high a figure for the surface layers of the sediments, the greater compaction in the lower layers will doubtless raise the average to or above the figure chosen by Stabler, who based his assumption on the experimental work whose results are published by the United States Geological Survey and the United States Reclamation Service. At 85 pounds to the cubic foot, a square mile of the sediment 1 foot thick would weigh 1,184,832 short tons. Multiplying by the percentage of zinc and lead in each deposit and by the area of each class, we get 2,000,000,000 short tons of zinc and 4,000,000,000 short tons of lead in the red clay 1 foot deep over its total area and 1,200,000,000 tons of zinc and 64,000,000 tons of lead in 1 foot of blue mud over its total area.

So far the calculations have been based upon reasonably accurate data. If, now, we wish to arrive at some conception of the total lead and zinc locked up in the pelagic and terrigenous deposits of the sea, it is necessary to make estimates as to the depth of the sediments. The red clay is made up of meteoric particles, volcanic and other terrestrial dusts, chemical sediments, and remains of pelagic life; but as the latter were primarily derived from mineral matter carried in solution in the sea water they will, in the estimates given below, be included with the chemical sediments. The blue mud includes not only the material enumerated above, but also detrital material carried out from the land areas. Basing his estimates on the average composition and total volume of river waters discharged into the sea and assuming 83,472,000 years as the period of sedimentation, Clarke[1] gives 191 feet as the thickness of the chemical sediments, the red-clay area being excluded, since chemical precipitation is regarded as insignificant in that area. For the mechanical sediments or silts Clarke gives an estimated thickness of 550 feet, making a thickness of, say, 750 feet for the terrigenous deposits of these two classes. To this estimate an addition should be made for the terrestrial and meteoric dusts. Perhaps 50 feet will be a fair figure for the addition from these sources, which would give 800 feet as an estimate of the total thickness of the terrestrial sediments.

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[1] Stabler, Herman, Some stream waters of the western United States, with chapters on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274, p. 164, 1911.

Murray[2] gives the following as the average composition of the red clay and the blue mud:

Average composition of red clay and blue mud.

	Red clay.		Blue mud.	
Carbonate of lime:				
Pelagic Foraminifera	4.77		7.52	
Bottom-living Foraminifera	.59		1.75	
Other organisms	1.34		3.21	
		6.70		12.48
Residue:				
Siliceous organisms	2.39		3.27	
Minerals	5.56		22.48	
Fine washings	85.35		61.77	
		93.30		87.52
		100.00		100.00

The larger percentage of "fine washings" (decomposed and unidentifiable minerals, consisting largely of fine clay or silicate of alumina) in the red clay testifies to its slow accumulation, which gives time for mineral decomposition, and the larger percentage of "minerals" (undecomposed volcanic material) in the blue mud is evidence of its more rapid accumulation. The percentage of red clay composed of remains of organisms, both lime carbonate and siliceous (9.09 per cent), as compared with the percentage of such remains in the blue mud (15.75 per cent) is to be interpreted as due to slower accumulation in the red clay of the remains of pelagic organisms rather than faster accumulation of the inorganic material, for the percentage of lime carbonate in the red clay decreases very rapidly below 2,200 fathoms, owing to greater solution of the calcareous tests in falling through greater depths of the sea water. Apparently, therefore, nothing in the comparative mechanical analyses of the red clay and the blue mud will serve to give a workable estimate of their relative rates of deposition.

The only observations bearing on the rate of deposition of materials on the sea floor are those of Peake, quoted by Murray.[3] A telegraph cable raised from a depth of 2,000 fathoms was found to be covered with Globigerina ooze after having lain 13 years. It was concluded that ooze equal to the thickness of the cable (1 inch) had been deposited in about 10 years. Assuming, with Clarke, that deposition has been going on for 83,472,000 years, and, with Seelheim, that the compacted layers would be more than twice as dense as the upper inch, we should get a depth of Globigerina ooze of approximately 300,000 feet, which is manifestly excessive, either for general or for local pelagic sedimentation.

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[1] Clarke, F. W., Some geochemical statistics: Am. Philos. Soc. Proc., vol. 51, p. 232, 1912.

[2] Murray, John, and Renard, A. F., Deep-sea deposits: Voyage of H. M. S. *Challenger*, pp. 197, 232, 1891.

[3] Murray, John, and Hjort, Johan, The depths of the ocean, pp. 169-170, London, 1912.

Another line of observation offers some clue to the relative rate of deposition of the red clay and the blue mud, as well as of the Globigerina ooze. Murray says:[1]

> Magnetic or cosmic spherules were found in greatest abundance in the red clays of the central and southern Pacific; in short, in the deepest water, at points farthest removed from continental masses of land. When the magnetic particles are extracted from about a quart of the clay from these regions, it is usual to observe among these between 20 and 30 of the small black spherules, with or without metallic nuclei, and 5 or 6 of the brown magnetic spherules with crystalline structure.
>
> Again, if a quart of Globigerina ooze, pteropod ooze, diatom ooze, blue mud, or other terrigenous deposit, be examined in the same way as a red clay or radiolarian ooze from the deep region of the central Pacific, as a general rule no, or at most only one or two, magnetic spherules will be observed among the magnetic particles.

As the rain of cosmic or meteoric spherules must be practically the same over all parts of the sea as well as on the land, it would apparently follow from the foregoing that the deposition of the blue mud, etc., goes on 15 to 20 times as rapidly as the deposition of the red clay. If, therefore, the assumption of 800 feet, based on Clarke's calculations for the thickness of the terrigenous deposits, be good, the rate of deposition of the red clay would indicate for it a thickness between 40 and 50 feet.

If we bear in mind Clarke's estimate of approximately 200 feet for the depth of chemical sedimentation in the terrigenous area, as well as the evidently much slower accumulation of chemical sediments in the pelagic area, and if we remember further that over 90 per cent of the red clay consists of minerals and fine clay resulting from the decomposition of meteoric and terrestrial dust, it seems likely that the contributions of dust particles would make up in good part for the deficiency of chemical sediments, and that 100 feet may be a reasonable minimum estimate of the thickness of the red clay. This estimate may be compared with the anonymous estimate of 500 feet quoted by Lane.[2]

Accepting these estimates of 800 feet thickness for the blue mud and 100 feet for the red clay and applying them to the total lead and zinc in 1 foot thickness of those deposits, we get approximately 400,000,000,000 short tons of lead and 200,000,000,000 tons of zinc in the red clay and 51,000,000,000 tons of lead and 9,600,000,000,000 tons of zinc in the blue mud, a staggering total of 451,000,000,000 tons of lead and 9,800,000,000,000 tons of zinc in two classes of sediments covering about half the area of the deep-sea deposits. Without doubt similar composite analyses of the other classes of terrigenous deposits would show that they too contain analogous quantities of the metals. These figures, of course, are mere approximations and, like Clarke's estimates of the thickness of the terrigenous clays, represent orders of magnitude only. Their usefulness consists in forcing the realization that the sediments are great storehouses of the metals.

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[1] Murray, John, and Renard, A. F., Deep-sea deposits: Voyage of H. M. S. *Challenger*, pp. 332–333,

[2] Lane, A. C., Meteor dust as a measure of geologic time: Science, vol. 37, p. 674, 1913.

ORIGIN OF THE METALS IN THE OCEANIC SEDIMENTS.

It is pertinent to inquire as to the source of the metals in the oceanic deposits. Murray believes that the greater part of the pelagic red clay is material of volcanic or meteoric origin, consisting of dust which has been carried out to sea, and that comparatively little of it is water-borne sediment or has been derived by chemical precipitation from the sea. Under this conception the inference would be that the metals had their source in the volcanic and meteoric dusts, and this conclusion is drawn by Murray.[1] This origin may be true for the red clay; but it seems to the writer that the total percentage of arsenic, nickel, cobalt, copper, lead, and zinc in the red clay (0.0637 per cent) as compared with the total percentage of these metals (0.0981 per cent) in the blue mud (which is unquestionably in large part of clastic origin and was derived from the land masses and in which the volcanic and meteoric contributions have been much diluted by the water-borne clastic sediments) shows that the metalliferous constituents have been added in a quantity greater than that of the clastic material. Hence we must conclude either that the water-borne clastic material is more than equally metal bearing with the volcanic and meteoric material, or that the two kinds of sediments, derived from diverse sources and holding reasonably similar quantities of the metals, have had those metals added in part at least from a third source—that is, the sea. The latter alternative is rendered plausible by the known presence of zinc and lead in sea water at different places, in corals, in the ashes of seaweed, and lastly in the manganese nodules, the analysis of which is cited above. This alternative is further strengthened by the fact that the analysis of a composite sample of silt from the Mississippi Delta (see p. 72), mud derived from a drainage basin producing fully half the lead and zinc of the United States, shows that mud to contain only one-half as much lead and one-eighth as much zinc as the terrigenous blue mud deposited at great distances from the land. These observations are in accord with the conclusions of Luther Wagoner,[1] who, in studying deep-sea dredgings, found that "The general result of the assays indicates that the bed of the Atlantic, whether coastal or pelagic, carries appreciable amounts of gold and silver, and that the deep-sea bottom is relatively richer in gold than that nearer the shore line." The metals, therefore, seem to be transported in solution and not as integral parts of the silt. Moreover, the carbonaceous silts do not seem to be effective as precipitants of the metals.

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[1] Murray, John, and Renard, A. F., Deep-sea deposits: Voyage of H. M. S. *Challenger*, p. 377, 1891.

Murray[2] suggests that the colloidal character of the clay particle enables it to attract to and incorporate with itself fine particles of other substances, a phenomenon which we now recognize as adsorption. Sullivan[3] has shown that the natural silicates precipitate the metals from solutions of salts by interchange of bases, a process in which adsorption plays little if any part. Murray and Irvine[4] conclude:

> That wherever organic matter is in process of decomposition in sea water, a reduction of the sulphur salts of the alkalies and alkaline earths contained therein takes place, with the result that the alkalinity of the water is increased.
>
> That when the above reaction takes place in the water at the bottom, or associated with the deposit on the bottom, a portion, and sometimes all, of the sulphur in the sea-water salts is removed and deposited as sulphide of iron, thus giving the characteristic blue-black color to the terrigenous deposits known as blue muds.

The sea, as we have seen, contains in solution copper, lead, zinc, and other metals which may be abstracted from the water and deposited with the sediments by the above-mentioned or analogous processes. The terrigenous deposits contain nearly as high a percentage of clayey material as do the pelagic deposits, and about twice as high a percentage of organic remains as the pelagic deposits. The heavier percentage of the metals in the blue mud is thus easily accounted for.

METALS DISSEMINATED IN THE ROCKS OF THE REGION.

Metal content of the Archean rocks of Missouri.—The analyses by Robertson, cited below, which were made on unusually large quantities of material, show that the pre-Cambrian crystalline rocks of the St. Francis Mountains contain notable percentages of lead, zinc, and copper. The ore body at the Einstein silver mine, as described by Winslow,[5] was a true vein associated with basic dikes in the

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[1] Wagoner, Luther, The presence of gold and silver in deep-sea dredgings: Am. Inst. Min. Eng. Trans., vol. 38, p. 705, 1908.

[2] Murray, John, and Renard, A. F., Deep-sea deposits: Voyage of H. M. S. *Challenger*, footnote, p. 196, 1891.

[3] Sullivan, E. C., The interaction between minerals and water solutions, with special reference to geologic phenomena: U. S. Geol. Survey Bull. 312, pp. 37-64, 1907.

[4] Murray, John, and Irvine, Robert, On the chemical changes which take place in the composition of sea water associated with blue muds on the floor of the ocean: Roy. Soc. Edinburgh Trans., vol. 37, p. 500, 1895.

[5] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 701-702, 1894.

Archean granite and carried argentiferous galena. Buckley[1] cites other veins showing lead and zinc in the crystalline area.

Metal content of Archean rocks.[a]

[J. D. Robertson, analyst.]

	Zinc.	Lead.	Copper.
	Per cent.	*Per cent.*	*Per cent.*
Granite, Graniteville, St. Francois County	0.00240	0.00272	0.01040
	.00300	.00204	.01000
Granite, Clearwater, Reynolds County	.00139	.00204	.00240
	.00160	.00197	.00290
Porphyry, Hogan, Iron County	.01760	.00496	.00400
	.01650	.00509	.00300
Diabase, Skrainka, Madison County	.01600	.00680	.00720
	.01360	.00612	.00720
Total	.07209	.03174	.04710
Average	.00301	.00397	.00590
Ratio of zinc to lead=1:0.440; ratio of zinc to copper=1:0.653.			

[a] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, p. 479, 1894.

Metal content of the Cambrian and Ordovician dolomites.—The Cambrian and Ordovician dolomites of the Ozark region also contain lead and zinc in measurable quantities, according to the following analyses by Robertson:

Metal content of "Silurian" [Cambrian and Ordovician] magnesian limestones in Missouri.[a]

[J. D. Robertson, analyst.]

	Zinc.	Lead.	Copper.
	Per cent.	*Per cent.*	*Per cent.*
Jefferson County, Frumet mines	0.01528	0.00041	0.00208
	.01536	.00051	.00200
Miller County, Rothwell diggings	.00080	.00156	.00040
	.00024	.00143	.00064
Pettis County	.00040	Trace.	.00048
	.00040	Trace.	.00108
St. Francois County, Desloge mine	.00528	.00129	.00240
	.00503	.00129	.00256
St. Francois County, railway tunnel, Valle mines	.00408	.00102	.00056
	.00400	.00132	.00192
Wright County, Mansfield	.00016	.00136	.00056
	Trace.	.00130	.00048
Total	.05103	.01149	.01516
Average	.00425	.00096	.00126
Ratio of zinc to lead=1:0.224; ratio of zinc to copper=1:0.297.			

[a] Winslow, Arthur, op. cit., p. 480.

A series of limestones from Iowa was analyzed by Dr. J. B. Weems,[2] who used the large-quantity methods of Robertson, with the results given in the following table:

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[1] Buckley, E. R., Lead and zinc deposits of the Ozark region: Types of ore deposits, p. 105, 1911.

[2] Calvin, Samuel, and Bain, H. F., Geology of Dubuque County: Iowa Geol. Survey, vol. 10, p. 567, 1900.

Metal content of limestones and dolomites in Iowa.

[J. B. Weems, analyst.]

	Zinc.	Lead.
	Per cent.	*Per cent.*
Blue galena limestone from Halpin mine	0.00072	0.00587
Niagara limestone, Cascade, Iowa	.00016	.00525
Lower buff beds, Sageville, Iowa	....	.00465
"Trenton" limestone, Sageville, Iowa	....	.00567
"Upper thin beds," sec. 33, Dubuque Township	.00040	.00280
Niagara limestone, Sherrill's mound	....	.00060
Galena limestone below cap rock (first opening), Tibey quarry	....	.00101
Lime-burning rock, Eagle Point	....	.00143
Non lime-burning rock, Eagle Point	.00136	.00204
Total	.00264	.02932
Average	.00029	.00326
Ratio of zinc to lead=1:11.1.		

Metal content of the Mississippian limestones.—The Mississippian limestones, when analyzed by the large-quantity methods of Robertson, show appreciable quantities of copper, lead, and zinc.

Metal content of Mississippian limestones in Missouri.[a]

[J. D. Robertson, analyst.]

	Zinc.	Lead.	Copper.
	Per cent.	*Per cent.*	*Per cent.*
Greene County, Phenix quarry	Trace.	0.00061	0.00048
	Trace.	Trace.	Trace.
Jasper County, Carthage quarry	0.00152	.00068	.00048
	.00160	.00048	.00048
Jasper County, Joplin, bluff on Turkey Creek	.00128	.00084	.00096
	.00120	.00088	.00048
	.00134	.00027	....
Jasper County, Webb City, near Sucker Flat	.00088	.00260	.00128
	.00120	.00272	.00120
Lawrence County, half a mile south of Aurora	.00072	.00346	.00880
	.00080	.00333	.00865
Pettis County, Sedalia quarry	Trace.	Trace.	.00012
	Trace.	Trace.	.00040
Pike County, Louisiana quarry	.00248	.00068	.00256
	.00255	.00068	.00240
Total	.01557	.01723	.02829
Average	.001038	.001149	.00202
Ratio of zinc to lead=1:1.107; ratio of zinc to copper=1:1.817.			

[a] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, p. 481, 1894.

Metal content of the Pennsylvanian shales.—Chemical analyses have been recently cited[1] to show that carbonaceous shales of Pennsylvanian age in Missouri and of Ordovician (Maquoketa) age in the upper Mississippi Valley region carry lead and zinc in measurable quantities as an original constituent of the shale. At most of the places cited, however, the close association of these disseminations with deposits plainly of later origin and their proximity to the base of the shale formation, together with the difficulty of distinguishing such minute later deposits of lead and zinc in a dark substance, like carbonaceous shale, do not incline one to view these disseminations as examples of sedigenetic deposits. Considerations that affect the transportation for long distances of lead and zinc in water carrying carbonaceous matter and increase the probability that these deposits are secondary have been discussed on pages 69–70.

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[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, vol. 9, p. 221, 1909. Cox, G. H., The origin of the lead and zinc ores of the upper Mississippi Valley district: Econ. Geology, vol. 6, p. 587, 1911.

It is possible that analyses, similar to Robertson's, of the shales of Pennsylvanian age around the border of the uplift would yield appreciable quantities of the metals. If investigation should prove the general presence of the metals in these shales it seems safe to suppose that the more resistant sulphides of copper, nickel, cobalt, and iron will compose a much larger percentage of the total in these rocks than in the limestones. The more resistant sulphides are last to be taken into solution, as has been shown on page 44. As the Pennsylvanian shales were laid down over nearly all the dome, it seems likely that the crystalline rocks were the only available source of metals. As these rocks were in preceding periods leached of their more soluble metals and furnished the metal content of the Cambrian, Ordovician, and Mississippian rocks, it seems only reasonable to suppose that we should find that in the Pennsylvanian shales the more resistant sulphides exceed in amount the less resistant sulphides, or at least that we should find them in greater proportion in these than in the earlier sediments. It is interesting to note in this connection that a single qualitative analysis of Pennsylvanian shale from the Sullivan mine shaft at Miami, Okla., made in the chemical laboratory of the United States Geological Survey by E. C. Sullivan, determined the presence not only of a small quantity of zinc but of an even larger quantity of nickel.

Comparison of the metal content of different rocks.—The localities from which the samples came, the care used in sampling, and the special methods of analysis are described in the volume of the Missouri Geological Survey cited in connection with the analyses. Some of the samples were collected at considerable distances from known bodies of ore and a few from points entirely outside the mining districts.

Though the large-quantity analyses do not show the iron content of the Archean crystalline rocks or of the limestones, it is certain that both classes of rocks contain much more iron than copper, lead, or zinc. It should be remembered that the crystalline rocks contain the famous deposits of Iron Mountain and Pilot Knob.

The average zinc, lead, and copper content, as shown by the analyses of the crystalline rocks of the Cambrian and Ordovician dolomites and of the Mississippian limestones of Missouri, as well as the ratios of the metals to each other in each of the different groups of rocks named, is a matter of much interest. The large-quantity analyses of Robertson, quoted below, show that on the average the total content of zinc, lead, and copper in the crystalline rocks is almost three times as large as in the Cambrian and Ordovician dolomites, and nearly five times as large as that in the Mississippian limestones. Zinc is on the average more than twice as plentiful in the crystalline rocks as in the Cambrian and Ordovician dolomites and nearly nine times as plentiful as in the Mississippian limestones. Lead is on the average more than four times as plentiful in the crystalline rocks as it is in the Cambrian and Ordovician dolomites and not quite four times as plentiful as in the Mississippian limestones. Copper is on the average almost five times as plentiful in the crystalline rocks as in the Cambrian and Ordovician dolomites, but hardly three times as plentiful as in the Mississippian limestones. In the crystalline rocks there is on the average less than half as much lead as zinc and about two-thirds as much copper as zinc. In the Cambrian and Ordovician dolomites there is a little less than one-fourth as much lead as zinc and a little less than one-third as much copper as zinc. In the Mississippian limestones there is on the average one-tenth more lead than zinc and eight-tenths more copper than zinc. These variations in the metal content of the rocks are strictly consistent, as will be shown later, if we assume that the metals were originally disseminated in the crystalline rocks and were dissolved, carried out to sea, and deposited in disseminated form in the limestones forming at the bottom of the sea in different geologic periods.

CONCLUSIONS.

As pointed out in the preceding pages, it is not maintained in this paper that all the zinc and lead in the Ozark deposits came originally from the igneous rocks of the St. Francis Mountains, but it is held that so far as the present segregation is concerned the metals were derived from the Cambrian and Ordovician limestones. The St. Francis Mountains doubtless contributed to the metal content of these limestones as well as to the other sediments found on the sea floor about the pre-Cambrian uplift, but, as indicated in the discussion of the origin of the metals in the deep-sea sediments (pp. 76–77), it is thought that a notable portion of the metal content of the Cambrian and Ordovician limestones as well as of the other sediments was contributed directly by the sea water itself.

THE ORE SOLUTIONS.

SOLUTIONS IN GENERAL.

The properties of liquid solutions are continuous functions of their composition, calculated in terms of the pure substances of which they are composed. * * * Any solution is therefore completely characterized by stating the nature and proportion of the pure substances of which it is composed or into which it can be separated.[1]

The properties of a dilute salt solution are thus dependent upon those of its resulting free ions rather than on the properties of the dissolved salt as such. * * * The properties of salts in solution are merely the sum of the properties of their ions.[2]

The writer holds that the ore deposits of the Joplin region were precipitated from waters ascending under artesian pressure at or near the locality of deposition and that those waters were similar to waters now rising under similar conditions or in artesian wells in contiguous territory to the west. In order that these waters of the contiguous area may be easily studied and compared with the waters of the Joplin region and with the zinc-bearing waters of other regions it is desirable that their quantitative analyses be reduced to some system whereby their composition and properties may be readily interpreted. Such a system, based on the general principles stated by Ostwald and quoted above, has been used by Stabler[3] and has been developed more fully by Chase Palmer. This system can best be briefly explained by quotations and summaries made from matter presented by the author last mentioned. For a fuller discussion of the subject the reader is referred to the publications cited.

GEOCHEMICAL INTERPRETATION OF WATER ANALYSES.[4]

Terrestrial waters are essentially solutions of a few salts, and their chemical character, like that of solutions in general, depends on the nature and proportion of the substances they contain. The interpretation of the chemical character of a water from the results of analysis is necessarily uncertain and unsatisfactory if it is based merely on the amounts of the radicles determined. In analytical chemistry, as in other branches of the science, the chemist considers the inherent properties of the radicles of substances, and hence his statement of the results of a water analysis should be framed in accordance with the chemical nature and the proportional amounts of the radicles determined in a solution of mixed salts. There is no lack of information concerning the amounts of the various materials dissolved in natural waters and the mutual relations of their parts. What the chemist especially needs is a form of statement that will adequately express these relations and disclose the true proportions of the radicles. * * *

Two forms of stating the amounts of mineral materials dissolved in water have been widely used. * * *

The older form, which represents the radicles as grouped together in arbitrary combinations, has by no means lost all adherents. It seems to be held in especial favor by the engineer because it gives the amount of dissolved material in terms which enable him to determine the corresponding amounts of substances necessary to fit a water for special industrial uses. The geologist, however, long ago realized that this form of expressing the chemical character of a water is inadequate to the exacting demands of research and has resorted to the form of statement in which the amounts of the radicles determined are given as independent units. In other words, he has practically abandoned a form of chemical expression and has adopted instead a statement of physical results. Chemical literature furnishes abundant evidence that the statement of water analyses in a form which does not recognize the proportional reaction capacity of the radicles fails to show the chemical character of the waters. Waters differing widely in character may be grouped together as similar if the classification is based on the preponderance of any radicle that may be considered as dominant in a solution of salts or on the apparent predominance of two or more radicles selected merely because they contribute largely to the weight of the mixture. Such classifications may be interesting from several points of view, but they are unreliable guides to the solution of geologic problems involving chemical processes. Furthermore, chemists whose attention is fixed on the physical weights of the radicles, which are assumed to be free and independent, may easily fail to observe important facts concerning the chemical character of waters, especially facts relating to geology.

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[1] Ostwald, W., The fundamental principles of chemistry, pp. 97, 119, 1909.

[2] Ostwald, W., The scientific foundations of analytical chemistry, p. 51, 1908.

[3] Stabler, Herman, Some stream waters of the western United States, with chapters on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274, pp. 165-181, 1911.

[4] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, pp. 5-12, 1911.

One advantage of the ionic form of stating water analyses is that it assigns weights directly to the chemically active parts of the dissolved substances instead of using those parts to build imaginary structures. The statement of the amounts of the radicles, however, indicates only the chemical composition of a water, not its character, for the physical weight of a radicle is no criterion of its chemical value in a system of dissolved salts such as exists in water. On the other hand, if the radicles are considered not as matter subject only to the law of gravitation, but rather as individuals acting together under the law of equivalent combining weights, contributing their proportional shares to the final balance of the system, the meaning of the results of a mineral analysis of water can be expressed clearly and precisely.

The reaction capacities of the radicles of the salts dissolved in water are the quotients obtained by dividing the weight of each radicle by its corresponding equivalent combining weight, or by multiplying by the reciprocal of its equivalent combining weight. * * *

The weights of the radicles have thus been resolved to values which are chemically measurable by a common standard. The unit of measurement is the milligram of hydrogen, in conformity with the international acceptance of hydrogen as the standard of reaction capacity. * * * As "milligram equivalents" chemists have long used reacting values to determine the accuracy of analyses.

To compare accurately two analyses expressed in reacting values they should be reduced to the same degree of concentration, that is, of dilution. This is readily accomplished by expressing the reacting values of each radicle as a percentage of the sum total of the reacting value of all radicles.

PROPERTIES OF NATURAL WATERS.

Nearly all terrestrial waters have two general properties, salinity and alkalinity, on whose relative proportions their fundamental characters depend. Salinity is caused by salts that are not hydrolyzed; alkalinity is attributed to free alkaline bases produced by the hydrolytic action of water on solutions of bicarbonates and on solutions of salts of other weak acids.

All the positive radicles, including hydrogen, may participate in producing salinity; but of the negative radicles only those of the actively strong acids can perform a similar function. Likewise all the positive radicles may participate in producing alkalinity; but of the negative radicles only those of the weaker acids may participate. The principal strong acids in natural waters are represented by the sulphates, chlorides, and nitrates. The principal weak acids in such waters are indicated by the carbonates, sulphides, phosphates, etc. Since salinity depends on the combined activity of equal values of both positive and negative radicles, and since its degree is limited only by the reacting values of the strong acids, the full value of salinity is obtained by multiplying the total value of the strong acid radicles by 2.

The full value of alkalinity and at the same time due recognition of the parent substances which are the source of alkalinity can be obtained by doubling the values of the bases in excess of the values of the strong acids.

The positive radicles [bases] determined in a water analysis, in accordance with their properties, fall naturally into three groups, as follows:

[Primary bases.] Alkalies.

[Secondary bases.] Earths or alkaline earths.

[Tertiary bases.] Metals, including hydrogen.

The groups of positive radicles are measured by the sum of the reacting values of their members, and in accordance with the prevalence of the reacting values of the groups of positive radicles in the system, these special properties are possible, namely:

1. Primary salinity; that is, salinity not to exceed twice the sum of the reacting values of the radicles of the alkalies [or primary bases].

2. Secondary salinity; that is, the excess (if any) of salinity over primary salinity not to exceed twice the sum of the reacting values of the radicles of the alkaline earths [or secondary bases].

3. Tertiary salinity; that is, the excess (if any) of salinity over primary and secondary salinity.

4. Primary alkalinity; that is, the excess (if any) of twice the sum of the reacting values of the alkalies [primary bases] over salinity.

5. Secondary alkalinity; that is, the excess (if any) of twice the sum of the reacting values of the radicles of the alkaline earths [secondary bases] over secondary alkalinity.[1]

Palmer[2] has recently restated somewhat more concisely the conclusions stated in the second paragraph under the heading "Properties of natural waters," as follows:

All the radicles of the alkalies and alkaline earths tend to form alkaline solutions, but only the strong acid radicles (sulphate, chloride, nitrate) can overcome this tendency and render an alkaline solution neutral or saline. The sum of the reacting values of the strong acid radicles is therefore a measure of the salinity (saltness) of a natural water which is a solution of salts of strong and weak acids. The sum of the reacting values of the metallic radicles in excess of the values of the strong acids is a measure of the alkalinity of a water.

In considering the analyses here given it is found that in six waters, the mineral content of which was probably derived in part from the oxidation of metallic sulphides, there is an excess of the positive radicles of the primary, secondary, and tertiary groups over the radicles of the strong acids, an excess which is balanced by radicles of the weaker acids. The resulting property has been called "subalkalinity" by Stabler, or, in consonance with the terms used above, it may be called "tertiary alkalinity," that is, the excess (if any) of twice the sum of the reacting values of the radicles of the metals [or tertiary bases] over the tertiary salinity.

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[1] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, pp. 11-12, 1911.

[2] Stephenson, L. W., A deep well at Charleston, S. C., with a report on the mineralogy of the water by Chase Palmer: U. S. Geol. Survey Prof. Paper 90, p. 92, 1914.

> The character of natural waters with reference * * * to their solvent action on minerals with which they may come in contact, to sedimentary deposits that they are likely to form, * * * and to their chemical action in general can best be portrayed by a statement of as many of the * * * special properties above mentioned as may be found, expressed in percentages of their totality.[1]

If natural waters, which are dilute solutions of mixed salts, are regarded as homogeneous substances, then their inert or feebly active constituents, such as free carbon dioxide, free hydrogen sulphide, and colloids, may be considered as accessories not involved in the activities of the solution, upon which they are simply superimposed; hence they may be excluded from the percentage characterization of the water; and in the following interpretations of analyses of waters they have been so excluded.

Palmer[2] has given the reaction coefficients of a number of the more common bases and radicles in natural waters; he has shown in the tables a convenient method of setting down the reacting values and their percentage calculations; and he has also shown the geochemical interpretation of the waters by representing the properties of the radicles and bases grouped as percentage of primary, secondary, or tertiary alkalinity or salinity. In the accompanying tables of analyses, this plan, somewhat abbreviated, has been followed. The analyses are grouped by State and country of origin of the water, but each analysis bears its serial number in the synoptical chart, by which it may also be easily identified in the list of localities.

ACIDITY, NEUTRALITY, AND ALKALINITY OF WATERS.

Many chemical reactions turn upon the acidity or alkalinity of the solution, and in ore deposition certain minerals characterize deposits made by acid ore solutions and a different set of minerals characterizes deposits made by neutral or alkaline ore solutions. Dilute solutions that are nearly neutral and that contain alkaline-earthy carbonates and are in contact with air containing carbon dioxide, may at different times be slightly acid, neutral, or slightly alkaline, their character varying with variations in the temperature, in the pressure of carbon dioxide, and other conditions. The acidity or alkalinity is usually ascertained by adding to the solution certain organic substances called indicators, which assume one color in acid solutions and a markedly different color in alkaline solutions.

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[1] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, p. 12, 1911.

[2] Idem, pp. 8, 9, 13, and 14.

The difficulties in determining acidity or alkalinity by means of indicators have been recently set forth by Walker and Kay,[1] by Washburn,[2] and by Moir.[3] The following quotation is from Walker and Kay:

> Natural waters may be acid, neutral, or alkaline according to the substances which are dissolved in them. The acidity or alkalinity of water is usually determined by means of an indicator, but since different indicators yield different results, and as the selection of an indicator is largely a matter of individual habit, it not infrequently happens that one and the same sample of water is reported as acid by one analyst and as alkaline by another. * * *
>
> *Neutrality, acidity, and alkalinity.*—The properties which we include under the general term "acidity" are due to the presence of the acid ion, hydrion, $H^{\cdot}$, in water; the properties which we include under the general term "alkalinity" are due to the alkaline ion, hydroxidion, OH', in water. Absolutely pure water has these two opposed substances in chemically equivalent proportions, and is neutral, and all truly neutral solutions have the same concentration of hydrion and hydroxidion in them as pure water. The concentrations of the two ions are of course equal, and the following table contains the values given by A. A. Noyes for different temperatures:
>
> | | |
> |---|---|
> | 0° C | 0.30×10^{-7} normal. |
> | 18° C | 0.68×10^{-7} normal. |
> | 25° C | 0.91×10^{-7} normal. |
> | 100° C | 6.9×10^{-7} normal. |
>
> Now, according to the ionization theory, the product of the concentrations of hydrion and hydroxidion in any dilute solution must always be equal to the corresponding product of pure water at the same temperature. All solutions, then, with a hydrion concentration greater than 0.68×10^{-7} at 18° are acid, and the hydrion concentration may be taken as a measure of the extent of the acidity. All solutions with a smaller concentration of hydrion than 0.68×10^{-7} are alkaline, and the hydrion concentration may be taken likewise as a measure of alkalinity.
>
> *Relative acidity and alkalinity.*—For theoretical purposes this mode of stating acidity or alkalinity in terms of hydrion (or hydroxidion) concentration is convenient, but for the practical requirements of the water analyst it is unsuited, owing to the rapid variation with temperature, and also to the smallness of the concentrations dealt with.
>
> We therefore propose for practical purposes that the acidity or alkalinity of a solution be stated in terms of the acidity or alkalinity of ideally pure water at the same temperature. In short, we propose that (just as in the case of density, specific heat, and many other physical properties) water be taken as standard substance and that the acidity or alkalinity of all aqueous solutions be referred to it under the same conditions. We therefore take the acidity of pure water=1, and the alkalinity of pure water=1 at all temperatures, no matter what the actual value of the hydrion concentration may be. That the acidity and alkalinity of pure water should be each made equal to 1 is necessary, since neutral water can have no excess of either.
>
> Thus a water which has a hydrion concentration of 1.36×10^{-7} and a hydroxidion concentration of 0.34×10^{-7} at 18° would be stated to have a relative acidity of 2 and a relative alkalinity of 0.5. Under this system the product of relative acidity and

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[1] Walker, James, and Kay, S. A., The acidity and alkalinity of natural waters: Soc. Chem. Ind. Jour., vol. 31, pp. 1013-1016, 1912.

[2] Washburn, E. W., The significance of the term alkalinity in water analysis and the determination of alkalinity by means of indicators: Illinois Water-Supply Assoc. Proc. second meeting, pp. 93-101, 1910.

[3] Moir, James, The determination of the acidity or alkalinity of waters—a study in indicators: South Africa Chem., Met. and Mining Soc. Jour., vol. 14, pp. 114-118, 1913.

relative alkalinity must alawys be equal to 1, that being the value of the product for pure water. In practice the value of the relative acidity alone would be given for acid waters, and of relative alkalinity alone for alkaline waters. * * *

Relation between temporary hardness and acidity.—In contrast with pure water, which is neutral, distilled water, in equilibrium with air and free from all impurities except dissolved air, is acid. The only substance in the (pure) atmosphere which confers acidity on water is carbon dioxide, and the relative acidity of water in equilibrium with air may be calculated from known data to be about 20.

It is a common experience to find that ordinary distilled water has a marked acidity toward phenolphthalein, and as a rule the relative acidity will be found to exceed 20. This is due to it containing excess of carbon dioxide derived from the bicarbonates in the water which is being distilled.

Natural waters containing dissolved bicarbonates in addition to carbon dioxide may be neutral, alkaline, or acid. The degree of hydrolysis of the bicarbonate, which varies with the concentration of the carbon dioxide in the water, is the chief factor which determines the alkalinity (or acidity) and, for a given hardness, if the concentration of the carbon dioxide is fixed, the hydrolysis, and hence the alkalinity of the water, will have a perfectly definite value. If air free from carbon dioxide is passed through the water the concentration of the carbon dioxide in the water will ultimately become zero and the water will become alkaline.

Treatment with ordinary air, on the other hand, may either increase or diminish the alkalinity of the water. The concentration of the carbon dioxide in the water, whatever it may originally be, reaches a fixed value at equilibrium, and the "temporary" hardness of the water determines whether the ultimate state of the water will be neutral, alkaline, or acid. In other words, the relative alkalinity of the water, if it is in equilibrium with air, depends on the "temporary" hardness. If the "temporary" hardness of a natural water, commonly ascertained by measuring the so-called "alkalinity" with standard acid and methyl orange, is really due to bicarbonates alone, the relative alkalinity of the natural water, after it is brought into equilibrium with air, ought to be equal to that of a synthetic water of the same temporary hardness. * * *

Practical applications.—The method sketched out above is of importance as affording a means for determining the actual acidity or alkalinity of a water, and not merely the potential acidity or alkalinity as given by ordinary titration. It is on this actual state of the water that the rate of its action on metals, etc., depends. For example, a very soft natural water of relative acidity 1.3 had its acidity increased to 5.0 after mechanical filtration with addition of aluminium sulphate. The quantity of aluminium sulphate added was equivalent to not more than half the temporary (bicarbonate) hardness present in the original water, so that the filtered water still possessed temporary hardness and contained no free acid save carbonic acid, to excess of which the high relative acidity was due. Yet the effect of the increased acidity was to increase the action of the filtered water on lead to three times that of the unfiltered water, and render the supply for this reason undesirable. The same filtered water was found to act briskly on mixed deposits of rust and the carbonates of lime and magnesia, dissolving the latter and liberating the iron rust.

Washburn[1] points out the contradictory results at which we may arrive by the use of different indicators, and gives a table showing the results in practice with a number of indicators. Some indicators change color when the solution is slightly acid, others only when it is markedly acid. Some indicators are not affected by acid solutions, but change color when the solution becomes slightly alkaline, and still others change only when it is pronouncedly alkaline. In the table the results of treating the indicators with solutions of different degrees of acidity and alkalinity are arranged progressively, leading from those which are affected only by strongly acid solutions to those which are affected only by decidedly alkaline solutions. It is manifest that the neutrality of a solution can be determined only by taking the middle point in the change of an indicator which shows some variation in color throughout the range from slightly acid to neutral to slightly alkaline. Litmus is such an indicator, being red-violet in slightly acid solutions, violet in neutral solutions, and blue in slightly alkaline solutions. It is frequently difficult to determine the neutral tint of an indicator such as litmus, and Moir[1] has devised an ingenious apparatus consisting of two parallel-walled glass cells, the distance between the walls of which is equal. The cells are filled with the same litmus solution; to one is added a measured quantity of acid and to the other an equivalent quantity of alkali. They are then placed side by side and the tint observed by looking through both at once is obviously the same as that of a single solution at exactly its middle point. Manifestly this method can be used only with indicators that exhibit some change of color on each side of the neutral point.

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[1] Washburn, E. W., op. cit.

Cohn[2] mentions a useful combination of indicators for solutions not varying much from the neutrality point as follows:

> The mixture of methyl orange and phenolphthalein was recommended by Gawalowski as an excellent neutrality indicator. The neutral point is indicated by a lemon-yellow color. The slightest excess of either acid or alkali causes a change of color, the acid affording a deep pink, the alkali a fine red.

ANALYSES OF ZINC-BEARING AND RELATED WATERS.

SOURCES OF INFORMATION.

Almost all the water analyses that have been here cited as having a bearing on the genesis of ores in the Ozark region are analyses of sulphate waters—that is, of mine waters and so-called "alum" waters. It has seemed desirable to make a rather complete collection of analyses of waters of all classes known to contain zinc or lead. In the compilation of these analyses the following publications, among others, have been examined:

Foreign.

Carnot, A., Analyses des eaux minérales françaises: Annales des mines, 8th ser., vol. 7, pp. 79–144, 1885; 9th ser., vol. 6, pp. 355–457, 1894; 9th ser., vol. 16, p. 33–94, 1899.

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[1] Moir, James, op. cit., p. 116.

[2] Cohn, A. I., Indicators and test papers, their source, preparation, application, and tests for sensitiveness, 2d ed., p. 267, New York, 1907.

Deutsches Bäderbuch, Leipzig, 1907.

Jacquot, E., and Willm, E., Les eaux minérales de la France, Paris, 1894.

Jahrbücher des Nassauischen vereins für Naturkunde, Wiesbaden, vols. 27–66, 1873–1913.

Liversidge, A., Skey, W., and Gray, G., On the composition and properties of the mineral waters of Australasia: Australasian Assoc. Adv. Sci., vol. 7, pp. 87–108, 1898.

Raspe, Friedrich, Heilquellen-Analysen, Dresden, 1885.

American.

Adams, F. D., and LeRoy, O. E., The artesian and other deep wells on the island of Montreal: Canada Geol. Survey Ann. Rept., vol. 14, pt. O, 1905.

Anderson, Winslow, Mineral springs and health resorts of California, 1892.

Bailey, E. H. S., Special report on mineral waters: Kansas Univ. Geol. Survey, vol. 7, 1902.

Bartow, Edward, and others, The mineral content of Illinois waters: Illinois Geol. Survey Bull. 10, 1909.

Branner, J. C., The mineral waters of Arkansas: Arkansas Geol. Survey Ann. Rept. 1891, vol. 1, 1892.

Clapp, F. G., Underground waters of southern Maine: U. S. Geol. Survey Water-Supply Paper 223, 1909.

Clarke, F. W., The data of geochemistry, 2d ed.: U. S. Geol. Survey Bull. 491, 1911. Chapter 6 (pp. 168–205) gives analyses of many mineral wells and springs. On pp. 204–205 is given a list of published collections of water analyses which, in addition to the foregoing, includes several collections of analyses of foreign mineral waters.

——— Water analyses from the laboratory of the United States Geological Survey: U. S. Geol. Survey Water-Supply Paper 364, 1914.

Crook, J. K., The mineral waters of the United States, Philadelphia, 1899.

Deussen, Alexander, Geology and underground waters of the southeastern part of the Texas Coastal Plain: U. S. Geol. Survey Water-Supply Paper 335, 1914.

Ducloux, E. H., Aguas minerales alcalinas de la República Argentina: Revista del Museo de La Plata, vol. 14, pp. 9–52, 1907.

Ducloux, E. H. and L. H., Las aguas minerales de los valles de Hualfín y otros de la Provincia de Catamarca: Revista del Museo de La Plata, vol. 16, pp. 51–120, 1909.

Fuller, M. L., Contributions to the hydrology of eastern United States, 1903: U. S. Geol. Survey Water-Supply Paper 102, 1904.

——— Contributions to the hydrology of eastern United States, 1904: U. S. Geol. Survey Water-Supply Paper 110, 1905.

——— Underground-water papers, 1910: U. S. Geol. Survey Water-Supply Paper 258, 1911.

Fuller, M. L., and Clapp, F. G., The underground waters of southwestern Ohio, with a discussion of the chemical character of the waters by R. B. Dole: U. S. Geol. Survey Water-Supply Paper 259, 1912.

Gordon, C. H., Geology and underground waters of northeastern Texas: U. S. Geol. Survey Water-Supply Paper 276, 1911.

——— Geology and underground waters of the Wichita region, north-central Texas: U. S. Geol. Survey Water-Supply Paper 317, 1913.

Gould, C. N., Geology and water resources of Oklahoma: U. S. Geol. Survey Water-Supply Paper 148, 1905.

Hall, C. W., and others, Geology and underground waters of southern Minnesota: U. S. Geol. Survey Water-Supply Paper 256, 1911.

Harris, G. D., Veatch, A. C., and others, A report on the underground waters of Louisiana: Louisiana Geol. Survey Bull. 1, 1905.

HAYWOOD, J. K., Mineral waters of the United States: U. S. Dept. Agr. Bur. Chemistry Bull. 91, 1905.

HEADDEN, W. P., Colorado irrigation waters and their changes: Colorado Agr. Exp. Sta. Bull. 82, 1903.

——— The Doughty springs, a group of radium-bearing springs on the North Fork of the Gunnison River, Delta County, Colo.: Colorado Sci. Soc. Proc., vol. 8, pp. 1–30, 1905.

——— Notes on some mineral springs: Colorado Sci. Soc. Proc., vol. 9, pp. 259–272, 1909.

KELLY, CLYDE, and ANSPACH, E. V., A preliminary study of the waters of the Jemez Plateau, N. Mex.: New Mexico Univ. Bull. 71, 1913.

LANE, A. C., Lower Michigan mineral waters: U. S. Geol. Survey Water-Supply Paper 31, 1899.

LEE, H. A., Mineral springs: Colorado Bur. Mines Ann. Rept. for 1897, pp. 145–154, 1898.

LEE, W. T., Water resources of the Rio Grande valley in New Mexico and their development: U. S. Geol. Survey Water-Supply Paper 188, 1907.

LOEW, OSCAR, Analyses of mineral springs and minerals: U. S. Geog. Surveys W. 100th Mer., vol. 3, pp. 613–637, 1875.

——— Report on the alkaline lakes, thermal springs, mineral springs, and brackish waters of southern California and adjacent country: U. S. Geog. Surveys W. 100th Mer. Ann. Rept. 1876, Appendix H 3, pp. 188–199, 1876.

MCCALLIE, S. W., A preliminary report on the underground waters of Georgia: Georgia Geol. Survey Bull. 15, 1908.

——— A preliminary report on the mineral springs of Georgia: Georgia Geol. Survey Bull. 20, 1913.

MATSON, G. C., Water resources of the Blue Grass region, Kentucky, with a chapter on the quality of the waters, by Chase Palmer: U. S. Geol. Survey Water-Supply Paper 233, 1909.

NORTON, W. H., Artesian wells of Iowa: Iowa Geol. Survey, vol. 6, pp. 115–428, 1897.

NORTON, W. H., and others, Underground water resources of Iowa: U. S. Geol. Survey Water-Supply Paper 293, 1912.

ORTON, EDWARD, The rock waters of Ohio: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 4, pp. 633–717, 1899.

PALMER, CHASE. See also Matson, G. C.

——— Mineralogy of waters from artesian wells at Charleston, S. C.: U. S. Geol. Survey Prof. Paper 90, 1914.

——— The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911.

PARKER, H. N., Quality of the water supplies of Kansas: U. S. Geol. Survey Water-Supply Paper 273, 1911.

PEALE, A. C., Lists and analyses of the mineral springs of the United States: U. S. Geol. Survey Bull. 32, 1886.

PETER, A. M., Kentucky Agr. Exper. Sta. Ann. Repts. 9–24.

PETER, ROBERT, Kentucky Geol. Survey Chem. Repts. 1–4.

PRATT, J. H., Mineral waters: North Carolina Geol. and Econ. Survey Econ. Paper 15, pp. 74–145, 1908.

SANFORD, SAMUEL, The underground water resources of the Coastal Plain province of Virginia: Virginia Geol. Survey Bull. 5, 1913.

SCHWEITZER, PAUL, A report on the mineral waters of Missouri: Missouri Geol. Survey, vol. 3, 1892.

SHEPARD, E. M., Underground waters of Missouri, their geology and utilization: U. S. Geol. Survey Water-Supply Paper 195, 1907.

SHEPARD, J. H., The artesian waters of South Dakota: South Dakota Agr. Coll. and Exper. Sta. Bull. 41, 1895.

SIEBENTHAL, C. E., Geology and water resources of the San Luis Valley, Colo.: U. S. Geol. Survey Water-Supply Paper 240, 1910.

SKINNER, W. W., American mineral waters; the New England States: U. S. Dept. Agr. Bur. Chemistry Bull. 139, 1911.

SLOSSON, E. E., Water analyses: Wyoming Agr. Exper. Sta. Bull. 24, 1895.

VAN WINKLE, WALTON, Quality of the surface waters of Washington: U. S. Geol. Survey Water-Supply Paper 339, 1914.

——— Quality of the surface waters of Oregon: U. S. Geol. Survey Water-Supply Paper 363, 1914.

VEATCH, A. C., Geology and underground water resources of northern Louisiana and southern Arkansas: U. S. Geol. Survey Prof. Paper 46, 1906.

WARING, G. A., Springs of California: U. S. Geol. Survey Water-Supply Paper 338, 1915.

WINCHELL, A. N., Petrology and mineral resources of Jackson and Josephine counties, Oreg.: The mineral resources of Oregon, vol. 1, No. 5, pp. 82–107, Oregon Bur. Mines and Geology, 1914.

FOREIGN MINERAL WATERS (TABLE 1).

The Deutsches Bäderbuch contains about 650 analyses of mineral waters of Germany, 35 of which record lead or zinc, or both, either in the water itself or in the sediment deposited by the water. Twenty-one of the most modern of these analyses have been recalculated to the geochemical basis for comparison with the water of the Joplin region and are given in the accompanying tables. Of these 21 analyses 11 show determinable quantities of the metals, 7 show traces only, and 9 show lead or zinc in the spring deposit. Of the total 21 analyses, 17 are of primary waters—that is, waters in which the alkali bases exceed the alkaline-earth bases, among them the salt waters. All the analyses of foreign mineral waters given in the table are taken from the Bäderbuch with the exception of five, the authority for which is stated in the list. The analysis of the water of Néris-les-Bains, by Willm, has been supplemented by a determination of fluorine by Gouvenain and by determinations of the metals by Carles.[1]

MINERAL WATERS OF EASTERN, CENTRAL, AND SOUTHERN STATES (TABLE 2).

Peale gives 20 analyses of waters containing zinc or lead, 17 of which are sulphate of "alum" waters carrying measurable quantities of zinc and 3 of which are carbonate waters. For reasons which will appear later it has not been deemed necessary to incorporate more than three or four analyses of sulphate waters in the table, as such waters result from the oxidation of metallic sulphides at shallow depths and will, of course, contain zinc if the original sulphide contained zinc.

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[1] Carles, M. P., Présence de la baryte dans les eaux minérales sulphatées: Annales chim. anal., vol. 7, pp. 91-93, 1902.

Crook gives eight analyses as containing either measurable quantities or traces of lead or zinc. Most of these are given by Peale.

The analyses of mineral waters from the Eastern, Central, and Southern States, with the exceptions noted in the list, are given by Peale.

MINERAL WATERS OF KENTUCKY (TABLE 3).

The mineral springs of Kentucky have long been famous, and the waters of many of them have been chemically analyzed, the results being published in reports made by Robert Peter and A. M. Peter. The analyses made prior to 1896 do not show the zinc content of these waters, but all Kentucky waters analyzed since that time have been examined for zinc. The total number of analyses of waters, qualitative and quantitative, published between 1896 and 1913 by the Kentucky Agricultural Experiment Station is 392, and 89 of these showed zinc in traces or in measurable quantity. Of the 392 waters analyzed, 95 contained hydrogen sulphide and 11 others probably contained it, though the gas had escaped before the sample reached the laboratory. Of the waters containing hydrogen sulphide, 49 carried sodium sulphide. Of the 89 waters containing zinc, 36 contained hydrogen sulphide and 17 contained sodium sulphide. These figures are of interest in connection with the notes on pages 48–49 in relation to the solution of zinc sulphide by excess of alkaline sulphides. The location of most of these wells and springs is shown on the accompanying sketch map of Kentucky (fig. 6).

Most of the analyses given in the reports of the Kentucky Agricultural Experiment Station are qualitative, but 7 quantitative analyses of waters containing zinc are given in the accompanying table (pp. 120–123) together with 5 quantitative analyses made by Chase Palmer,[1] of the United States Geological Survey, which are stated [2] to show traces of zinc, although such traces are not noted in the analyses as originally published. The analyses are included in A. M. Peter's list of well waters showing zinc. Peter has very kindly permitted the use of the following unpublished paper describing the chemical methods used by him in determining the zinc content of mineral waters and giving a list of 89 zinc-bearing waters that had been analyzed prior to 1911. Peter [3] has since published qualitative analyses of 17 additional waters containing zinc in traces or in measurable quantities.

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[1] Water resources of the Blue Grass region: U. S. Geol. Survey Water-Supply Paper 233, pp. 212-215, 1909.

[2] Oral communication by Chase Palmer.

[3] Peter, A. M., Averitt, S. D., and Sheed, O. M., Analyses of mineral and potable waters: Kentucky Agr. Exper. Sta. Twenty-fourth Ann. Rept., for 1911, pp. 329-346.

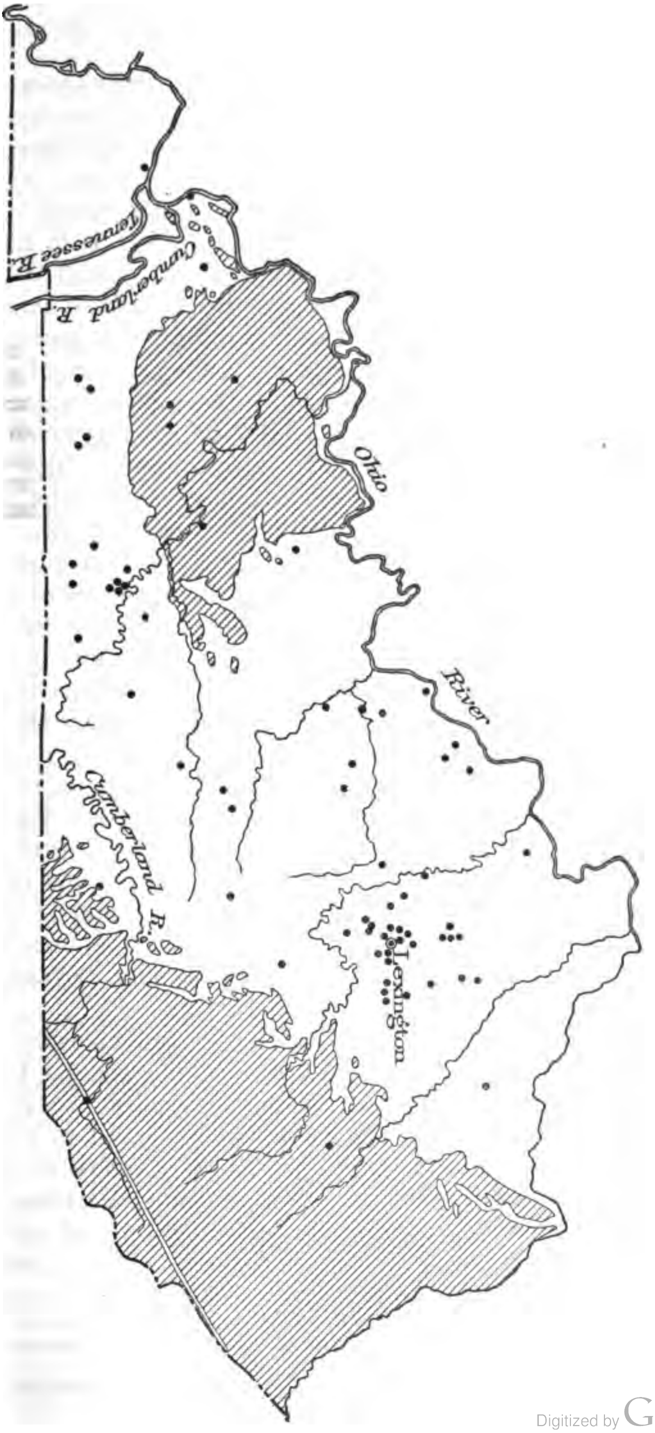

FIGURE 6.—Map of Kentucky showing location of zinc-bearing wells and springs. The shaded parts represent areas of Pennsylvanian rocks.

THE OCCURRENCE OF ZINC IN KENTUCKY MINERAL WATERS.

By A. M. PETER.[1]

Zinc is one of the metals that rarely appear in analyses of mineral waters. Indeed, I can not cite any American analysis in which it is shown, except those made by the Kentucky Experiment Station. On looking through Walton's "Mineral springs of the United States and Canada" (2d ed., 1874), which contains a very good collection of the older analyses, some 300 or 400 in number, I do not find its presence stated in any of the waters described, though Walton says, in the chapter on chemical constituents, that "traces of zinc * * * are sometimes detected." Haywood and Smith[2] report analyses of 55 commercial waters, in none of which is the presence of zinc noted, and the method of analysis followed by these chemists does not provide for the detection of that metal. In the "Deutsches Bäderbuch," published in Leipzig in 1907, which contains analyses of about 650 mineral waters from the German Empire, I find zinc reported in only 18 waters and in the sinter deposited from 11 others.

These facts would seem to point to the rarity of zinc as a constituent of mineral waters, so I thought it might be of interest to present this note of work done in the laboratory of the Kentucky Agricultural Experiment Station, which shows that zinc is of common occurrence in certain classes of Kentucky waters and that its presence may be detected in many of them by a method of analysis not especially refined. Since 1896, in which year I first noted the presence of zinc in a Kentucky mineral water, it has been our practice to test for that metal in the waters submitted to us for analysis. Upon looking through the annual reports of the station from 1896 to 1910, I find the analyses of 392 samples of mineral water reported, and of these, 72 show the presence of zinc in solution in the water and 17 in the sediment deposited from the sample on standing in the bottle, a total of 89 samples in which zinc was found, presumably derived from the water. Most of these analyses are qualitative.

In our usual procedure the test for zinc is made upon the same portion of water that is used for testing for iodine, bromine, borate, and soluble carbonate and for spectroscopic examination. For this purpose, one-half to 1 liter of the water is evaporated to dryness and the residue is extracted with a very small quantity of hot water. This concentrated solution is examined for soluble carbonate, borate, iodine, and bromine by appropriate tests and is tested spectroscopically. The residue not soluble in water is treated with a little hydrochloric acid and examined spectroscopically to detect strontium, lithium, calcium, etc., after which enough hydrochloric acid is added to decompose all the carbonates, and also a few drops of nitric acid, to oxidize ferrous compounds and organic matter, and the solution is brought to dryness for the separation of silica. The residue is taken up with hydrochloric acid and water, filtered, and ammonium hydroxide is added for the precipitation of ferric and aluminum hydrates. A precipitate is filtered out and the clear filtrate is acidified with acetic acid and treated with hydrogen sulphide. A precipitate of white sulphide here indicates zinc. It may be filtered, washed, burned to oxide, and weighed, the oxide being recognizable as zinc oxide from its color being lemon-yellow while hot, but white on cooling. We have made only a very few weighings, as the quantities found were very small. Those tried range from 0.0003 to 0.0065 gram zinc, calculated on the liter.

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[1] Paper read before Am. Chem. Soc., Louisville section, Apr. 16, 1910, but not submitted for publication by the society. Published here with certain additions by the author.

[2] Haywood, J. K., and Smith, B. H., U. S. Dept. Agr., Bur. Chemistry, Bull. 91, 1905.

Summarizing the samples according to geologic formations, we have 1 sample from the Quaternary, 5 from the "Coal Measures" (Pennsylvanian), 25 from the Mississippian, 3 from the Devonian, 6 from the Silurian, and 49 from the Ordovician. This classification is not exact, because it is made according to the surface geology of the counties without reference to the depth of the well. But I think it serves to show that it is the water from the limestone formations that carries zinc.

Classifying the samples according to the character of the water, we have 37 samples from sulphur waters, mostly salt sulphur containing metallic sulphide, 20 from saline waters, including sulphated saline waters, 19 from alkaline calcium carbonate waters, including those also containing sodium carbonate, 7 from chalybeate waters containing ferrous carbonate, and 6 not classified. Of the 89 samples, zinc was detected in the clear water of 68; in the remaining 21 it was detected only in the sediment which had formed in the bottle after standing.

It is interesting to note, also, that the zinc in the sediment of the saline waters, most of which come from the limestones of the Ordovician formations, is usually in the form of sulphide.

The character of the 89 Kentucky mineral waters is shown in the following table:

Kentucky mineral waters containing zinc.

[Analyses made in laboratory of Kentucky Agricultural Experiment Station and published in annual reports indicated in second column.]

County.	No. of annual report.	Page.	Laboratory No.	Depth of well (feet).	Total solids (grams per liter).	Zinc content.	Character of water.
Allen	17	179	14479		1.317	Trace	Moderately strong chalybeate.
Do	17	179	14598		1.383	do	Weak sulphur; some H_2S.
Do	18	227	14790		36.792	do	Very strong alkaline saline sulphur; Na_2S; some H_2S.
Anderson	13	xxx	7001	110	11.375	Trace of ZnS in sediment	Saline.
Bell	19	262	17092	95	.113	Trace	Very pure water.
Bourbon	12	xxii	5934		13.951	Small quantity of $ZnCO_3$	Strong saline.
Do	23	324	25851	90	.51	Trace of $ZnCO_3$	An average well water.
Bullitt	19	263	17089	8	7.469	Trace	Saline water; sulphates mostly.
Do	19	263	17221	50	7.906	Marked trace; zinc in sediment	Zinc and free sulphur in sediment; some H_2S.
Do	19	264	17222		.226	Trace	Usual quantity of mineral matter.
Do	19	264	17226	100	13.955	do	Good saline.
Butler	15	322	10069		.42	A little ZnS in sediment	Weak alkaline calcic.
Carroll	16	289	11704	98	3.318	Trace	Saline sulphur, slightly alkaline; some H_2S.
Do	16	289	a 12097	741	3.306	Trace of $ZnCO_3$	Mild alkaline saline sulphur; 22 parts per million H_2S.
Do	16	290	12098	180	7.221	Some $ZnCO_3$	Saline.
Christian	9	xxi	a 3564		3.026	ZnS in sediment	Strong salt sulphur; Na_2S; 63.4 parts per million H_2S.
Do	19	265	14989	105	8.471	Trace	Saline sulphur; H_2S.
Do	21	489	25173		.83	do	Weak saline.
Do	16	291	12069	134	4.842	Notable quantity of ZnS in sediment	Salt sulphur; 90 parts per million H_2S; Na_2S.
Do	16	292	12089	280	3.735	Marked trace	Saline; some H_2S.
Clark	19	265	17118	142	3.625	do	Moderately strong saline sulphur; H_2S; Na_2S.
Do	21	490	25208	65	.457	Trace	Free sulphur in sediment; a little H_2S.
Do	22	416	25356	165	3.808	Trace of $ZnCO_3$	Carbonated saline.
Fayette	13	xxvi	6494	212	.717	Some ZnS in sediment	Alkaline calcic; a little H_2S.
Do	13	xxxi	7075	180	10.425	A little ZnS in sediment	Saline.
Do	14	287	a 8136	250	12.47	Trace of ZnS in sediment	Alkaline saline.
Do	16	293	11722	126	.374	Trace	Slightly alkaline.
Do	16	293	11726a	95	.452	Trace of $ZnCO_3$	Alkaline calcic.
Do	16	294	11945	225	1.196	Very marked trace	Alkaline saline.
Do	16	297	12075	225	.976	Trace of ZnS	Alkaline calcic.
Do	16	297	12077		2.45	Some ZnS in sediment	Wholesome saline.
Do	16	297	a 12144	165	.373	4.5 parts per million ZnO	Alkaline calcic.
Do	16	298	12968	75	.566	A little ZnS in sediment	Weak alkaline sulphur; a little H_2S.
Do	17	182	14609	75	2.151	Marked trace; ZnS in sediment	Weak alkaline sulphur; some H_2S; Na_2S.
Do	18	230	14876	204	17.490	Marked trace of ZnS	Saline sulphur; Na_2S.
Do	20	199	17475	123	.739	Trace of $ZnCO_3$	Sodium chloride with $CaCO_3$ and $MgCO_3$.
Do	21	492	25140	108	.48	do	Alkaline saline.
Do	22	417	25309	68	.524	do	Strong alkaline, weak sulphur; very little H_2S.
Do	23	324	25967	160	5.768	do	Moderately strong salt.
Do	17	180	14504	126	.320	Marked trace	Alkaline.

Franklin	11	xxviii	4933		2.126	Notable quantity of ZnO in sediment	Alkaline saline.
Do	13	xxvii	6646		1.275	Some ZnS in sediment	Alkaline carbonated; a little H_2S.
Green	17	184	14588	50	5.323	Some Zn; ZnS in sediment	Alkaline saline sulphur; some H_2S; Na_2S.
Harrison	21	493	25212		5.223	Trace	Moderately strong saline.
Do	23	325	25933	95	6.12	Small quantity of $ZnCO_3$	Moderately strong salt sulphur; a little H_2S.
Hopkins	19	267	17123	50	.695	Trace	Chlorides, carbonates, and sulphates.
Do	19	267	17223	27	3.464	do	Weak saline sulphur; some H_2S.
Jefferson	16	299	[a] 12093	Spring.	.3024	do	Weak calcic.
Jessamine	13	xxxiii	7178	180	5.11	Some ZnS	Weak saline.
Do	14	293	8580	100	3.221	Notable quantity of ZnS in sediment	Mild saline sulphur; 12.7 parts per million H_2S.
Do	17	185	14421		13.25	Marked trace	Saline.
Do	19	267	17224	60	15.950	Trace	Good salt sulphur; H_2S; Na_2S.
Do	20	203	17795	75	.408	Trace of $ZnCO_3$	Alkaline saline.
Do	20	203	17796	114	3.687	Notable quantity of ZnS	Weak alkaline saline sulphur; H_2S.
Do	21	495	[a] 17994	60	16.525	Trace	Good salt sulphur; H_2S; Na_2S.
Lincoln	18	232	14684	50	53.418	do	Strong brine.
Livingston	22	421	25530	106	.400	Trace of $ZnCO_3$	Average well water.
Logan	17	187	14506		3.326	Trace	Strong alkaline saline sulphur; Na_2S; 84 parts per million H_2S.
Do	21	498	25072		.394	Faint trace	Weak alkaline carbonated.
McCracken	22	422	25655		.140	Trace of $ZnCO_3$	Alkaline chalybeate; over three-quarters of solids is $FeCO_3$.
Muhlenberg	21	499	25123		8.038	Faint trace of $ZnCO_3$	Chalybeate with rather large quantity $MgSO_4$.
Nelson	11	xxvi	4612		22.57	Notable quantity of $ZnCO_3$	Strong saline.
Do	16	302	13092	100	.711	Trace	Alkaline calcic; trace of H_2S.
Oldham	16	303	[a] 11614	Spring.	.247	0.5 part per million $ZnCO_3$	Calcic magnesian.
Do	21	500	25073	45	2.753	Decided trace	Magnesium sulphate.
Do	21	500	25074	45	1.177	Distinct trace	Do.
Scott	19	274	17069	24	4.681	Some	Moderately strong saline.
Do	20	205	[a] 17844	192	1.096	Trace	Weak alkaline saline.
Do	21	501	25097	72	10.152	Trace of $ZnCO_3$	Rather strong salt.
Do	21	502	25189	120	9.112	Small quantity of $ZnCO_3$	Rather strong salt; some H_2S.
Simpson	16	304	11676		.429	Trace of $ZnCO_3$	Moderately strong chalybeate.
Do	17	191	14502	37	1.569	ZnS in sediment	Saline sulphur; H_2S; some Na_2S.
Taylor	16	305	12132	30	1.65	Trace of $ZnCO_3$	Calcic.
Do	19	275	17005	39	1.288	Trace	Very weak chalybeate.
Todd	16	306	12173		.513	Trace of $ZnCO_3$	Calcic chalybeate.
Do	18	232	14682	42	.462	do	Alkaline; all carbonates, including sodium carbonate.
Do	18	233	14841	53	3.212	Small quantity of ZnS	Good alkaline saline sulphur; some H_2S; Na_2S.
Do	18	234	14864		1.224	A little ZnS	Alkaline saline sulphur; some H_2S; Na_2S.
Warren	16	307	11467	130	18.327	Some ZnS in sediment	Very strong saline sulphur; 1,310 parts per million H_2S; Na_2S.
Do	17	193	14628	61	.59	Trace	Slightly alkaline, weak sulphur; some H_2S; Na_2S.
Do	20	207	[a] 17832		20.165	A little	Very strong alkaline saline sulphur; Na_2S.
Do	21	503	25107	62½	.365	A little $ZnCO_3$	Ordinary surface water.
Wayne	14	295	8755	75	1.194	A little ZnS in sediment	Sulphosaline.
Woodford	13	xxxi	7025		3.646	Trace of ZnS in sediment	Mild alkaline sulphur; notable quantity H_2S.
Do	18	235	14715	180	6.452	A little $ZnCO_3$	Strong saline; some H_2S.
Do	18	236	14734	120	14.616	A little ZnS	Strong saline sulphur; H_2S; Na_2S.
Do	19	277	14897		9.366	Trace of ZnS	Blue Lick water; a little H_2S.
Do	19	278	17220	200	17.57	do	Rather strong saline; a little H_2S.
Do	23	328	25974		.69	Trace of $ZnCO_3$	Weak chalybeate.

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[a] The quantitative analysis of this water is given in the table of analyses, pp. 120–123.

WELL, SPRING, AND MINE WATERS OF MISSOURI (TABLE 4).

Two published reports deal especially with the mineral waters of Missouri—Schweitzer's report on the mineral waters of the State and Shepard's report on the underground waters, both cited in the list given above. Many of the analyses included in Shepard's paper were originally published in earlier water-supply papers, issued by the United States Geological Survey, and the earlier publications are the ones cited in the accompanying tables. The analyses taken from these sources have been supplemented by four analyses given in the chapter on the lead and zinc deposits of the Ozark region, contributed by E. R. Buckley to the volume entitled "Types of ore deposits," as well as by several analyses collected by W. S. Tangier Smith in connection with earlier work on the district and by a number of commercial analyses communicated by Prof. W. George Waring and others. It has thus fortunately been possible to get together a fairly large collection of analyses of Missouri waters. These analyses cover practically all classes of waters in the Joplin district—limestone springs, sulphate springs (probably contaminated by mine drainage), mine waters, and deep-well waters. Although in more than half these analyses no test was made for zinc or lead, some samples of sediment deposited from waters that were not themselves tested for these metals were assayed for this report and have on analysis shown lead or zinc or both.

SPRING WATERS OF ARKANSAS (TABLE 5).

At the town of Sulphur Springs, in the northwest corner of Arkansas, several springs rise to the surface in the valley of Butler Creek. One of these is known as White Sulphur Spring and another as Black Sulphur Spring. The analysis of water from the former was made by Prof. W. George Waring. Another analysis, by Dr. A. E. Menke, has been published in the Arkansas Geological Survey's report on mineral waters, but as its source is called simply the "Sulphur Spring," it is uncertain from which spring the sample was taken. In its geochemical characteristics the water analyzed by Menke differs considerably from the water analyzed by Waring, and they fall a considerable distance apart in the synoptical table. Sulphide sediment from each spring was analyzed by Waring and showed the presence of lead, zinc, copper, and iron. Crystallized pyrite, calcite, and quartz are also forming in these sediments. These interesting sediments are discussed more fully on pages 185–187.

WELL AND SPRING WATERS OF KANSAS (TABLE 6).

Kansas waters are described in Bailey's report and also in the United States Geological Survey water-supply paper by Parker listed on page 90. Except an analysis of water from a limestone spring and one of water from a spring containing zinc sulphate, the analyses cited from Kansas are of artesian (but not flowing) wells, most of them serving as sources of municipal water supply. When so used, the water is usually pumped into a surface reservoir and in this reservoir a dark sulphury sediment settles out of the water. All samples of this sediment examined contained weighable quantities of lead and zinc. Thus several of the waters can be said to carry these metals, although the waters were not tested for them when the analyses were made. These precipitates and their bearing on the genesis of the ore deposits are discussed in greater detail on pages 162–173.

WELL AND MINE WATERS OF OKLAHOMA (TABLE 7).

No report dealing with the waters of the eastern part of Oklahoma has yet been published, and it has therefore been necessary to compile such commercial analyses as are available. Nine of these are given in the table, together with analyses of three mine waters. The water from the Church-Mabon mine, north of Miami, in common with water from the other mines in this region, is charged with hydrogen sulphide and when classified by its properties according to the geochemical system falls alongside the water from the Nowata artesian well, which it very closely resembles. The water from the Chapman & Lennan mine, which is not far from the Church-Mabon mine and at the same geologic horizon, as sampled when the mine was first opened, is likewise a sulphur water, but differs from the water of the Church-Mabon mine in showing considerable sulphate salinity, indicating some surface oxidation, an indication which is corroborated by the higher lime-magnesia ratio and by the reported occurrence of stringy masses of sulphur bacteria in the water. In the classification it falls between waters from the deep wells at Nevada and Clinton, Mo. A second analysis of this water was made three months later, pumping having been continuous during the interval. This pumping had lowered the ground-water level so that surrounding mines were draining to the Chapman & Lennan mine, the deepest in the region. A comparison of the analyses shows a very pronounced change in the character of the water. When first sampled it was a primary water in which the alkali metals were predominant, but when the second sample was taken the water had changed to a secondary water, in which the alkaline-earth bases were predominant. There was a corresponding decrease in the chloride and sulphate radicles, which gave place to carbonate radicle, and in the content of hydrogen sulphide, which had been pronounced when the first sample was taken but was no longer evident. Attention is here directed to the position of these mine waters in the geochemical classification, for they will be discussed later as having a decided bearing on the theory of ore genesis presented in this paper.

Waters from the Radium well at Claremore, the Whitaker Park well at Pryor Creek, and the waterworks well at Vinita, show traces of lead and zinc, and sediments from these wells and from the waterworks well at Afton yield measurable quantities of lead and zinc. The Claremore and Nowata well waters are salt to the taste. Dr. E. H. Keiser, reporting under date of July 29, 1903, the analysis of the water of the Radium well at Claremore, says:

> I find that this water is highly charged with hydrogen sulphide gas. * * * The water when first drawn has a green-yellowish color. On standing, a black sediment collects on the bottom of the vessel, and if the water is exposed to the air a white precipitate of sediment slowly forms throughout the entire body of water. This formation of a white precipitate on standing is due to the liberation of finely divided sulphur from the gas (hydrogen sulphide) in the water. The black sediment that settles out is chiefly iron sulphide, but contains a little zinc sulphide. I was not able to find lead in the water.[1]

WELL, SPRING, AND MINE WATERS OF COLORADO (TABLE 8).

Of the ten analyses of zinc-bearing waters from Colorado, five were made by Dr. W. P. Headden, three by the United States Geological Survey, and the others were made by chemists indicated in the list. The analyses comprise waters from hot and cold springs, deep mines, a surface stream, and a sulphate well, whose water corresponds closely to mine water and was probably contaminated by mine water. The widely separated positions of the two analyses of the water of Geyser mine in the synoptical table are noteworthy, the water from the 2,000-foot level (p. 149) having the primary or alkali bases predominant, whereas that from the 500-foot level (p. 151) has the secondary or alkaline-earth bases predominant. The analyses of the Poncha Hot Springs and of the Hot Spring No. 1 at Wagon Wheel Gap fall very close together in the synoptical table (p. 149). Zinc was determined in the deposit from the water of each spring.

WELL, SPRING, AND MINE WATERS OF MICHIGAN, MONTANA, NEVADA, AND CALIFORNIA (TABLE 9).

With the exception of the water of one hot spring the waters analyzed from Michigan, Montana, Nevada, and California are deep-mine waters, most of which were supposed to be below the reach of surface or oxidizing influences. They were collected for their bearing on the genesis of the particular ore deposits with which they are associated. The water from the 3,095-foot level of the Tamarack mine of Michigan and from the 1,800-foot level of the Gagnon mine of Montana fall side by side in the synoptical table and resemble each other very closely, the principal difference (p. 152) being the larger content of sulphate radicle in the water of the Gagnon mine. In both, calcium chloride is the principal constituent. The water from the 2,200-foot level of the Green Mountain mine, Montana, resembles the Gagnon water, except that 78 per cent of the acid radicles consist of sulphate and calcium sulphate is the chief constituent, thus indicating a large component of surface oxidizing waters. Both the Montana mines are in the Butte district and both the waters have a faintly alkaline reaction. The water from the 2,316-foot bore hole in the Mizpah mine at Tonopah, Nev., contains an excess of the sulphate radicle, indicating surface origin, with primary or alkaline bases predominant, and resembles very closely the water from the Lullusquelle, which it adjoins in the synoptical table (p. 151). The water from the 400-foot level of the Federal Loan mine was collected by Lindgren,[1] who has recently commented upon it as follows:

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[1] Advertising circular of Claremore Radium Wells Co.

> Some years ago, in a report on the gold quartz veins of Nevada City and Grass Valley, Cal. (U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 121, 1896) I presented an analysis of an ascending spring found in the Federal Loan mine which carried some arsenic and hydrogen sulphide. At that time I held the opinion that this water might possibly have had some connection with the genesis of the vein, but it is now apparent that it is simply water of the general surface circulation which happened to find its way up on the vein and which dissolved certain constituents from it.

In the synoptical table (p. 151) this water falls between the water from the 500-foot level of the Geyser mine and water from the deep well of the Missouri Lead & Zinc Co. at Joplin, resembling the latter very closely.

The analysis of the water from Steamboat Springs, Nev.,[2] has been included in order to compare a hot alkaline sulphide-depositing water with the cold alkaline-saline sulphide-depositing water of the Joplin region. Classified by the geochemical system the water from Steamboat Springs finds its place among several cold springs of Colorado and Germany and a well water from Oklahoma. It has a considerably higher chloride salinity than any of these, however. In calculating this analysis the boron has been regarded as colloidal and the very small quantity of antimonate radicle reported has been disregarded. The water probably contains minute quantities of lead and zinc, as well as other metals, for these are found in the sinter deposit from which the springs emerge.

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[1] Lindgren, Waldemar, Mineral deposits, p. 42, footnote, 1913.

[2] Becker, G. F., Geology of the quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, p. 347, 1888.

Zinc-bearing and related waters included in the tables of analyses and in the synoptical table.

No. in synoptical table.	Source of water.	Locality.	Analyst.	Date of analysis.	Temperature of water.	Publication.
	FOREIGN.					
1	Lindenquelle	Birresborn, Germany	E. Hintz and L. Grünhut	1904	10.2° C.; 48.3° F.	Deutsches Bäderbuch, p. 87.
2	"Du Rocher" Spring	Puy-de-dome, France	M. Garrigou	1877		Compt. rend., vol. 84, p. 963, 1877.
4	Grosser Sprudel	Neuenahr, Germany	E. Hintz and L. Grünhut	1901	34.2° C.	Deutsches Bäderbuch, p. 102.
7	Arienheller Sprudel	Arienheller, Germany	E. Hintz	1897	22.4° C.	Deutsches Bäderbuch, p. 85.
9	Kainzen-(St. Antons) Quelle	Partenkirchen, Bavaria, Germany.	F. Hulna	1880	8° C.	Deutsches Bäderbuch, p. 14.
16	Rhenser Sprudel	Rhens, Germany	E. Hintz and L. Grünhut	1901	23.2° C.	Deutsches Bäderbuch, p. 108.
26	Niederbronn	Niederbronn, Germany	O. Haenle	1904	18° C.	Deutsches Bäderbuch, p. 202.
29	Solquelle "Bonifazius"	Berlin, Germany	R. and H. Fresenius	1889	13.2° C.	Deutsches Bäderbuch, p. 137.
37	Schönbornsprudel	Kissingen, Germany	E. von Gorup-Besanez and O. Liezenmayer.	1877		Deutsches Bäderbuch, p. 179.
39	Salztrinkquelle	Pyrmont, Germany	E. Hintz and L. Grünhut	1904	9.1° C.	Deutsches Bäderbuch, p. 361.
41	Elisabethbrunnen	Homburg, Germany	H. Fresenius	1901	10.6° C.	Deutsches Bäderbuch, p. 168.
43	Martinusquelle	Orb, Germany	E. Hintz and L. Grünhut	1906	10.6° C.	Deutsches Bäderbuch, p. 211.
44	Elisabethquelle	Kreuznach, Germany	R. and H. Fresenius	1893	12° C.	Deutsches Bäderbuch, p. 185.
47	Municipal water supply	Sydney, New South Wales	Sydney G. Walton	1909		Roy. Soc. New South Wales Jour. and Proc., pt. 2, pp. 148-156, 1909.
50	Viktoriaquelle	Kreuznach, Germany	R. and H. Fresenius	1893	13° C.	Deutsches Bäderbuch, p. 185.
52	Ocean	Mean of 77 analyses, Challenger samples.	W. Dittmar			Depths of the ocean, p. 176, Murray and Hjort, 1912.
54	Grossherzogin-Karolinenquelle	Kreuzburg, Germany	E. Hintz	1902	14° C.	Deutsches Bäderbuch, p. 271.
57	Antonienquelle	Warmbrunn, Germany	R. and H. Fresenius	1889	28° C.	Deutsches Bäderbuch, p. 34.
58	Carlsbad Sprudel	Carlsbad, Austria-Hungary	Prof. Ludwig	1879	166° F.	Carlsbad and its natural healing agents, p. 27, J. Kraus, London, 1880.
59	Néris-les-Bains	Allier, France	E. Willm	1891	50°-52.8° C.	Les eaux minérales de la France, pp. 113-115, 1894.
61	Lullusquelle	Hersfeld, Germany	E. Hintz and L. Grünhut	1905	10.5° C.	Deutsches Bäderbuch, p. 280.
62	Carolaquelle	Rappoltsweiler, Germany	R. Fresenius and E. Hintz	1888	16.9° C.	Deutsches Bäderbuch, p. 284.
63	Fontinalissprudel	Sinzig, Germany	E. Hintz and L. Grünhut	1905	14.7° C.	Deutsches Bäderbuch, p. 47.
85	Höllensprudel	Höllensprudel, Germany	E. Hintz	1902	14.5° C.	Deutsches Bäderbuch, p. 328.
94	Caspar-Heinrich-Quelle	Driburg, Germany	R. and H. Fresenius	1888	10.2° C.	Deutsches Bäderbuch, p. 308.
97	Eulenhöfer Quelle	Ronneburg, Germany	R. Fresenius and E. Hintz	1894	9.4° C.	Deutsches Bäderbuch, p. 371.
113	Cransac Spring	Rodez, France	E. Willm	1879	32°-48° C.	Les eaux minérales de la France, pp. 193-195, 1894.
119	Guber Spring	Bosnia				Mitchell's mineral and aerated waters, p. 24, 1913.

	EASTERN, CENTRAL, AND SOUTHERN STATES.					
8	Thompson Spring	Ashe County, N. C.	Henry Froehling	1885	....	Crook's Mineral springs of United States, p. 374.
28	Caddo oil well	Caddo Parish, La.	R. F. Gardner	1910	....	U. S. Geol. Survey Bull. (in press).
66	Minnequa Spring	Bradford County, Pa.	F. A. Genth	1875	47° ± F.	Pennsylvania Second Geol. Survey, vol. BB, p. 214, 1876.
67	Mida Mineral Spring	Mecklenburg County, N. C.	Robert C. Price	....	60° F.	Mining industry of North Carolina in 1907, p. 113.
73	Coppahaunk Spring	Waverly, Va.	Froehling and Robertson	....	....	Virginia Geol. Survey Bull. 5, p. 282, 1913.
93	Roanoke Red Sulphur Springs	Roanoke County, Va.	M. B. Hardin	1875	53°-60° F.	U. S. Geol. Survey Bull. 32, p. 67, 1886.
106	Johnson well	Oakville, Tex.	W. George Waring	1913	....	Made for this report.
107	King's mineral spring	Dallas, Ind.	W. A. Noyes	1901	....	Indiana Geol. Survey Twenty-sixth Ann. Rept., for 1901, p. 32, 1902.
112	Alleghany Spring	Montgomery County, Va.	F. A. Genth	....	56° F.	U. S. Geol. Survey Bull. 32, p. 58, 1886.
117	Bedford Alum Spring	Campbell County, Va.	M. B. Hardin	1877	56° F.	U. S. Geol. Survey Bull. 32, p. 59, 1886.
118	Rockbridge Alum Spring No. 2	Rockbridge County, Va.	do	1873	50°-56° F.	U. S. Geol. Survey Bull. 32, p. 65, 1886.
	KENTUCKY.					
19	Renfro well	Lexington	A. M. Peter, S. D. Averitt, and O. M. Shedd.	1911	....	Kentucky Agr. Exper. Sta. Twenty-fourth Ann. Rept., p. 335 (Lab. No. 36359).
21	Artesian well (741 feet)	Sanders	A. M. Peter	1903	....	Kentucky Agr. Exper. Sta. Sixteenth Ann. Rept., p. 289 (Lab. No. 12097).
22	Public well	Sadieville	Chase Palmer	1906	....	U. S. Geol. Survey Water-Supply Paper 233, pp. 214-215, 1909.
24	Bored well	Hopkinsville	A. M. Peter	1896	....	Kentucky Agr. Exper. Sta. Ninth Ann. Rept., p. XXII (Lab. No. 3564).
36	Estill well	do	Chase Palmer	1906	....	U. S. Geol. Survey Water-Supply Paper 233, pp. 212-213, 1909.
48	Sharp well	Nicholasville	S. D. Averitt and O. M. Shedd.	1908	....	Kentucky Agr. Exper. Sta. Twenty-first Ann. Rept., p. 495 (Lab. No. 17094).
49	Felix well	Chilesburg	Chase Palmer	1906	....	U. S. Geol. Survey Water-Supply Paper 233, p. 212, 1909.
53	School well	Warren County	A. M. Peter	1907	....	Kentucky Agr. Exper. Sta. Twentieth Ann. Rept., p. 207 (Lab. No. 17832).
65	Wilson well	Lexington County	Chase Palmer	1906	....	U. S. Geol. Survey Water-Supply Paper 233, p. 212, 1909.
74	Spring	Near Louisville	A. M. Peter	1903	....	Kentucky Agr. Exper. Sta. Sixteenth Ann. Rept., p. 299 (Lab. No. 12093).
75	Sayre well	Lexington	Chase Palmer	1906	....	U. S. Geol. Survey Water-Supply Paper 233, pp. 212-213, 1909.
83	Royal Magnesian Spring	Lagrange	A. M. Peter	1903	....	Kentucky Agr. Exper. Sta. Sixteenth Ann. Rept., p. 303 (Lab. No. 11614).
	MISSOURI.					
27	Nevada well (750 feet)	Nevada	J. D. Robertson	1892	....	Missouri Geol. Survey, vol. 3, pp. 121-122, 1892.
32	Waterworks well No. 2 (800 feet)	Clinton	A. E. Woodward	1892	....	Missouri Geol. Survey, vol. 3, pp. 118-120, 1892.
38	Silver well (to 1,100 feet)	St. Peters	A. H. Illinski	1909-1910	....	Missouri Bur. Geology and Mines, Forty-sixth Gen. Assembly, p. 67, 1909-10.

Zinc-bearing and related waters included in the tables of analyses and in the synoptical table—Continued.

No. in synoptical table.	Source of water.	Locality.	Analyst.	Date of analysis.	Temperature of water.	Publication.
	MISSOURI—continued.					
40	Britt well No. 3 (913 feet)	Clinton	J. D. Robertson	1892		Missouri Geol. Survey, vol. 3, pp. 120-121, 1892.
42	Artesian well No. 1	do	A. E. Woodward	1892		Missouri Geol. Survey, vol. 3, pp. 85-87, 1892.
51	Artesian well (1,505 feet)	Brunswick	do	1892		Missouri Geol. Survey, vol. 3, pp. 96-97, 1892.
55	Silver well (below 1,100 feet)	St. Peters	A. H. Illinski	1910		Missouri Bur. Geology and Mines, Forty-sixth Gen. Assembly, p. 67, 1909-10.
56	Belcher well (2,199 feet)	St. Louis	A. Litton	1860	23° C.=73.4° F.	St. Louis Acad. Sci. Trans., vol. 1, pp. 82-86, 1860.
64	Cornfield well	Carterville	Unknown	1902		U. S. Geol. Survey Water-Supply Paper 102, p. 405, 1904.
68	Missouri Lead & Zinc Co.'s well (1,387 feet).	Joplin	Cleveland and Millar	1902		U. S. Geol. Survey Water-Supply Paper 102, p. 406, 1904.
76	Waterworks well	Oronogo	W. George Waring	1905		Communicated.
82	Missouri Lead & Zinc Co.'s well (940 feet).	Joplin	Cleveland and Millar	1902		U. S. Geol. Survey Water-Supply Paper 102, p. 406, 1904.
84	Freeman Foundry well	do	do	1901	65° F.	Communicated.
86	Fulton Hospital well	Fulton	Northern Water Softener Co.	1911		Do.
87	Cox Spring	Thurman	H. N. Stokes	1902		U. S. Geol. Survey Water-Supply Paper 364, p. 14, 1914.
88	Harrington well	Carthage	V. H. Gottschalk	1911		Types of ore deposits, p. 124, 1911.
89	Providence well	Webb City	do	1911		Do.
91	Alba waterworks well	Alba	do	1911		Do.
92	Redell well (1,379 feet)	Joplin	H. N. Stokes	1902	66.5° F.	U. S. Geol. Survey Water-Supply Paper 364, p. 14, 1914.
95	Limekiln well	Ash Grove	A. F. Shattuck	1905		U. S. Geol. Survey Water-Supply Paper 195, p. 130, 1907.
96	Waterworks well	Webb City	W. George Waring	1910		Webb City Sentinel, July 27, 1910.
98	Freeman Foundry well	Joplin	Harrison Hale	1904		U. S. Geol. Survey Water-Supply Paper 195, p. 139, 1907.
99	Average of 10 mine waters	Southeastern Missouri	Missouri Geological Survey			Missouri Bur. Geology and Mines, vol. 9, p. 249, 1909.
100	Winslow mine water	Webb City	V. H. Gottschalk	1910		Types of ore deposits, p. 124, 1911.
101	B. & C. mine water	Joplin	H. N. Stokes	1902		U. S. Geol. Survey Water-Supply Paper 344, p. 36, 1914.
108	Sphalerite well (496 feet)	Aurora				U. S. Geol. Survey Water-Supply Paper 195, p. 144, 1907.
110	Lakeside Spring	Lakeside	W. P. Cleveland	1902		Communicated.

115	Missouri Zinc Fields mine water	Webb City	H. N. Stokes	1903	64° F	U. S. Geol. Survey Water-Supply Paper 344, p. 36, 1914.
116	Shoal Creek Spring	Joplin	W. F. Hillebrand	1891		Am. Jour. Sci., 3d ser., vol. 43, pp. 418–422, 1891.
	ARKANSAS.					
35	White Sulphur Spring	Sulphur Springs	W. George Waring	1914		Made for this report.
72	Sulphur Spring	do	A. E. Menke	1891		Arkansas Geol. Survey Ann. Rept. for 1891, vol. 2, p. 19.
	KANSAS.					
5	Waterworks deep well	Columbus	G. H. Failyer and J. T. Willard.	1886	24° C.; 75.2° F.	Kansas Univ. Geol. Survey, vol. 7, p. 262, 1902.
13	Waterworks well	Cherokee	E. H. S. Bailey and A. S. Hull.	1901	22° C.; 71.5° F.	Kansas Univ. Geol. Survey, vol. 7, p. 259, 1902.
33	Artesian well (621 feet)	Fort Scott	E. H. S. Bailey and E. W. Walter.	1901		Kansas Univ. Geol. Survey, vol. 7, p. 263, 1902.
78	Waterworks underground reservoir.	Pittsburg	W. George Waring	1912		Communicated.
90	Waterworks well (1,500 feet)	do	Dearborn Drug & Chemical Co.	1905		U. S. Geol. Survey Water-Supply Paper 273, p. 74, 1911.
102	Chico Spring	Galena	E. H. S. Bailey and E. McCallum.	1901	14.8° C.; 58.6° F	Kansas Univ. Geol. Survey, vol. 7, pp. 314–315, 1902.
103	Waterworks well No. 3	Pittsburg	W. George Waring	1912		Made for this report.
109	Cave Spring	Galena	E. H. S. Bailey and E. McCallum.	1901	15° C.; 59° F	Kansas Univ. Geol. Survey, vol. 7, pp. 313–314, 1902.
	OKLAHOMA.					
15	Frisco well	Vinita	Kennicott Water Softener Co	1903		Communicated.
18	Church mine water	Miami	R. C. Wells	1911		Made for this report.
20	Artesian well	Nowata	J. Robert Moechel	1905		Advertising pamphlet, republished in U. S. Geol. Survey Bull. 340, p. 228, 1908.
23	Old artesian well (600 feet)	Afton	Kennicott Water Softener Co			Communicated.
25	Whitaker Park well	Pryor Creek	W. George Waring	1912		Made for this report.
30	Chapman & Lennan mine water	Miami	do	1912		Communicated.
34	Ice plant well	do	John T. Wixford	1907		Do.
45	Brown well	Claremore	E. H. Keiser	1905		U. S. Geol. Survey Bull. 340, p. 227, 1908.
46	Radium well	do	do	1903		Do.
69	Town well	Bernice	W. George Waring	1913		Made for this report.
71	Chapman & Lennan mine water	Miami	do	1912		Communicated.
77	Deep well (889 feet)	Fairland	Oklahoma Agricultural and Mechanical College.			U. S. Geol. Survey Bull. 340, p. 227, 1908.
	COLORADO.					
3	Geyser mine water (2,000 feet)	Silver Cliff	W. F. Hillebrand	1895	80° F	U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 462, 1896.
6	Doughty Black Spring No. 1	Delta County	W. P. Headden	1904	17.5° C.; 63.5° F.	Colorado Sci. Soc. Proc., vol. 8, p. 9, 1905.
10	Poncha spring No. 1	Salida	Regis Chauvenet		90°–168° F	Colorado State Bur. Mines Rept. for 1897.
11	Hot spring No. 1	Wagon Wheel Gap	Colorado College	1904	135° F	Econ. Geology, vol. 8, p. 239, 1913.
12	Cold Sulphur Spring	Idaho Springs	W. T. Schaller	1907		U. S. Geol. Survey Prof. Paper 63, p. 164, 1908.
14	Doughty Drinking Spring No. 6	Delta County	W. P. Headden	1904		Colorado Sci. Soc. Proc., vol. 8, p. 15, 1905.
31	Yampa Spring	Glenwood Springs	Charles F. Chandler		120° F	U. S. Geol. Survey Mon. 31, p. 213, 1898.

Zinc-bearing and related waters included in the tables of analyses and in the synoptical table—Continued.

No. in synoptical table.	Source of water.	Locality.	Analyst.	Date of analysis.	Temperature of water.	Publication.
	COLORADO—continued.					
70	Royal Gorge Cold Spring	Canon City	W. P. Headden	1909	70° F	Colorado Sci. Soc. Proc., vol. 9, p. 264, 1909.
79	City water supply	Boulder	do	1902		Colorado Agr. Exper. Sta. Bull. 82, p. 61, 1903.
80	Geyser mine water (500 feet)	Silver Cliff	W. F. Hillebrand	1895		U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 461, 1896.
114	Railroad well	Black Hawk	W. P. Headden			Communicated.
	MICHIGAN, MONTANA, NEVADA, AND CALIFORNIA.					
17	Steamboat Springs	Steamboat Springs, Nev	W. H. Melville	1887	75°–84.5° C	U. S. Geol. Survey Mon. 13, p. 347, 1888.
60	Mizpah mine	Tonopah, Nev	R. C. Wells	1910		U. S. Geol. Survey Bull. 529, p. 63, 1913.
81	Federal Loan mine (400 feet)	Nevada City, Cal	W. F. Hillebrand	1895		U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 121, 1896.
104	Gagnon mine	Butte, Mont	do	1897		U. S. Geol. Survey Prof. Paper 74, p. 101, 1912.
105	Tamarack, jr., mine water	Calumet, Mich	George L. Heath	1905		Lake Superior Min. Inst. Proc., vol. 13, pp. 83–84, 1908.
111	Green Mountain mine	Butte, Mont	W. F. Hillebrand	1902		U. S. Geol. Survey Prof. Paper 74, p. 101, 1912.

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters.*

No. in synoptical table	1		2		4	
Source of water	Lindenquelle		"Du Rocher"		Grosser Sprudel.	
Temperature	10.2° C.=48.3° F				34.2° C.	
PROPERTIES.						
Primary salinity	14.0		33.0		11.2	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	56.2		55.2		46.2	
Secondary alkalinity	29.8		11.8		42.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	10.4		27.2		6.6	
Sulphate salinity	3.6		5.8		4.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	34.5	48.26	42.5	96.875	27.3	15.42
Potassium (K)	.4	.6060	1.0	2.272	1.2	.6555
Lithium (Li)	.1	.0671	.6	1.433	.1	.07450
Ammonium (NH_4)	.1	.08720	.0	.01468	.1	.0600
Alkalies	35.1		44.1		28.7	
Calcium (Ca)	2.5	3.534	3.2	7.376	7.4	4.212
Magnesium (Mg)	12.4	17.38	2.7	6.078	13.9	7.853
Barium (Ba)				Trace.		Trace.
Strontium (Sr)	.0	.0009		Trace.		Trace.
Earths	14.9		5.9		21.3	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)				Trace.		
Cobalt (Co)				Trace.		
Copper (Cu)		Trace.		Trace.		Trace.
Cadmium (Cd)						
Lead (Pb)				Trace.		Trace.
Zinc (Zn)	.0	.0040	.0	.01526		Trace.
Metals						
Sum of bases	50.0	69.94	50.0	114.1	50.0	28.28
Sulphate (SO_4)	1.8	2.508	2.9	6.641	2.3	1.284
Chloride (Cl)	5.2	7.241	13.6	31.00	3.3	1.859
Bromide (Br)	.0	.0051			.0	.0024
Iodide (I)	.0	.0001	.0	.0016		Trace.
Fluoride (F)						
Nitrate (NO_3)				Trace.		Trace.
Thiosulphate (S_2O_3)						
Strong acids	7.0		16.5		5.6	
Carbonate (CO_3)	43.0	60.18	33.5	76.42	44.4	25.11
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)	.0	.0005			.0	.0029
Phosphate (PO_4)	.0	.0007		Trace.	.0	.0124
Weak acids	43.0		33.5		44.4	
Sum of acids	50.0	69.94	50.0	114.0	50.0	28.28
Total value of reacting solids	100.0	139.98	100.0	228.0	100.0	56.56
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	5,471		8,636		2,223	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	31		273		33	
Total dissolved solids	5,502		8,909		2,256	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	2,555				1,150	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	7		9		16	
Source of water	Arienheller Sprudel.		"Kainzen-(St. Antons) Quelle."		Rhenser Sprudel.	
Temperature	22.4° C.		8° C.		23.2° C.	
PROPERTIES.						
Primary salinity	34.2		8.4		57.6	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	35.2		87.4		21.6	
Secondary alkalinity	30.6		4.2		20.8	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	29.4		2.0		37.8	
Sulphate salinity	4.6		6.2		19.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	33.7	44.43	47.3	10.09	38.9	44.06
Potassium (K)	.8	1.019	.5	.1045	.4	.4887
Lithium (Li)	.1	.1466	.0	.0015	.2	.1724
Ammonium (NH$_4$)	.1	.0989	.1	.0231	.1	.1388
Alkalies	34.7		47.9		39.6	
Calcium (Ca)	4.7	6.193	.9	.1863	5.7	6.409
Magnesium (Mg)	10.6	14.02	1.2	.2474	4.7	5.357
Barium (Ba)						Trace.
Strontium (Sr)			.0	.0008	.0	.0033
Earths	15.3		2.1		10.4	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.	.0	.0021		
Cadmium (Cd)						
Lead (Pb)			.0	.0004		
Zinc (Zn)		Trace.				Trace.
Metals						
Sum of bases	50.0	65.91	50.0	10.65	50.0	56.63
Sulphate (SO$_4$)	2.3	3.052	3.1	.6597	9.9	11.19
Chloride (Cl)	14.7	19.43	1.0	.2105	18.9	21.43
Bromide (Br)	.0	.0120	.0	.0002	.0	.0141
Iodide (I)	.0	.00001	.0	.0004	.0	.0001
Fluoride (F)						
Nitrate (NO$_3$)	.1	.0693	.1	.0231		Trace.
Thiosulphate (S$_2$O$_3$)						
Strong acids	17.1		4.2		28.8	
Carbonate (CO$_3$)	32.9	43.32	38.6	8.220	21.2	23.98
Sulphide (S)				Trace.		
Hydroxyl (OH)			7.2	1.54		
Arsenate (AsO$_4$)	.0	.0069			.0	.0016
Phosphate (PO$_4$)	.0	.0149			.0	.0139
Weak acids	32.9		45.8		21.2	
Sum of acids	50.0	65.91	50.0	10.65	50.0	56.63
Total value of reacting solids	100.0	131.8	100.0	21.30	100.0	113.3
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	4,867		610		3,993	
Colloids (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, BO$_3$, etc.)	32		11		38	
Total dissolved solids	4,899		621		4,031	
Gases:						
Hydrogen sulphide (H$_2$S)			Trace.			
Carbon dioxide (CO$_2$)	1,846		0		3,106	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	26		29		37	
Source of water	Niederbronn		Solquelle "Bonifazius."		Schönbornsprudel.	
Temperature	18° C		13.2° C			
PROPERTIES.						
Primary salinity	74.0		92.2		75.6	
Secondary salinity	3.8		6.8		10.8	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	22.2		1.0		13.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	76.0		95.8		73.6	
Sulphate salinity	1.8		3.2		12.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	32.7	53.31	46.0	410.5	36.5	160.7
Potassium (K)	4.2	6.848	.1	1.092	1.1	4.760
Lithium (Li)	.1	.0922	.0	.0362	.1	.3707
Ammonium (NH_4)			.0	.3411	.1	.4785
Alkalies	37.0		46.1		37.8	
Calcium (Ca)	10.5	17.11	1.8	15.56	7.4	32.44
Magnesium (Mg)	2.5	4.118	2.1	18.96	4.8	21.34
Barium (Ba)						Trace.
Strontium (Sr)	.0	.0169	.0	.2448		Trace.
Earths	13.0		3.9		12.2	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.		Trace.		
Cadmium (Cd)						
Lead (Pb)		Trace.				Trace.
Zinc (Zn)				Trace.		Trace.
Metals						
Sum of bases	50.0	81.50	50.0	446.7	50.0	220.1
Sulphate (SO_4)	.9	1.428	1.6	14.03	6.4	28.03
Chloride (Cl)	38.0	61.92	47.9	427.8	36.8	162.2
Bromide (Br)		Trace.	.0	.1506	.0	.0976
Iodide (I)		Trace.	.0	.0036		
Fluoride (F)						
Nitrate (NO_3)	.0	.0234				Trace.
Thiosulphate (S_2O_3)						
Strong acids	38.9		49.5		43.2	
Carbonate (CO_3)	11.1	18.12	.5	4.747	6.8	29.72
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)		Trace.				Trace.
Phosphate (PO_4)		Trace.	.0	.0026	.0	.0385
Weak acids	11.1		.5		6.8	
Sum of acids	50.0	81.50	50.0	446.7	50.0	220.1
Total value of reacting solids	100.0	163.00	100.0	893.4	100.0	440.2
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	5,262		26,211		13,730	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	45		32		33	
Total dissolved solids	5,307		26,243		13,763	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	121		4		1,647	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	39		41		43	
Source of water	Salztrinkquelle		Elisabethbrunnen.		Martinusquelle.	
Temperature	9.1° C		10.6° C.		10.6° C.	
PROPERTIES.						
Primary salinity	75.0		74.6		72.2	
Secondary salinity	12.0		12.8		14.6	
Tertiary salinity	......		......		......	
Primary alkalinity	......		......		......	
Secondary alkalinity	13.0		12.6		13.2	
Tertiary alkalinity	......		......		......	
	100.0		100.0		100.0	
Chloride salinity	69.6		87.0		74.6	
Sulphate salinity	17.4		.4		12.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	37.3	118.6	36.1	132.8	34.6	155.8
Potassium (K)	.2	.784	1.0	3.658	1.3	5.659
Lithium (Li)	.0	.0517	.1	.3563	.2	.6886
Ammonium (NH_4)	.0	.0835	.1	.2027	.0	.0951
Alkalies	37.5	......	37.3	......	36.1	......
Calcium (Ca)	8.3	26.55	9.4	34.51	10.4	46.88
Magnesium (Mg)	4.1	12.92	3.3	12.16	3.5	15.98
Barium (Ba)	......	......	.0	.0087	......	......
Strontium (Sr)	.1	.159	.0	.1964	.0	.1683
Earths	12.5	......	12.7	......	13.9	......
Iron (Fe)	......	......	......	......	......	......
Aluminum (Al)	......	......	......	......	......	......
Manganese (Mn)	......	......	......	......	......	......
Hydrogen (H)	......	......	......	......	......	......
Nickel (Ni)	......	Trace.	......	Trace.	......	......
Cobalt (Co)	......	......	......	......	......	......
Copper (Cu)	......	Trace.	......	Trace.	......	Trace.
Cadmium (Cd)	......	......	......	......	......	......
Lead (Pb)	......	......	......	......	......	......
Zinc (Zn)	.0	.0035	......	Trace.	.0	.0097
Metals	......	......	......	......	......	......
Sum of bases	50.0	159.2	50.0	183.9	50.0	225.3
Sulphate (SO_4)	8.7	27.77	.2	.4932	6.1	27.57
Chloride (Cl)	34.8	110.8	43.5	160.1	37.3	167.9
Bromide (Br)	.0	.0073	.0	.0287	.0	.0342
Iodide (I)	......	Trace.	.0	.0002	.0	.0001
Fluoride (F)	......	......	......	Trace.	......	......
Nitrate (NO_3)	.0	.0661	......	Trace.	.0	.0348
Thiosulphate (S_2O_3)	......	......	......	......	......	......
Strong acids	43.5	......	43.7	......	43.4	......
Carbonate (CO_3)	6.5	20.51	6.3	23.26	6.6	29.73
Sulphide (S)	......	......	......	......	......	......
Hydroxyl (OH)	......	......	......	......	......	......
Arsenate (AsO_4)	.0	.0001	.0	.002	.0	.0042
Phosphate (PO_4)	.0	.0005	.0	.0105	.0	.0025
Weak acids	6.5	......	6.3	......	6.6	......
Sum of acids	50.0	159.2	50.0	183.9	50.0	225.3
Total value of reacting solids	100.0	318.4	100.0	367.8	100.0	450.6
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	9,982		11,181		14,057	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	23		42		43	
Total dissolved solids	10,005		11,223		14,100	
Gases:						
Hydrogen sulphide (H_2S)	......		......		......	
Carbon dioxide (CO_2)	1,706		2,303		2,322	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	44		47		50	
Source of water	Elisabethquelle.		Sydney waterworks.		Viktoriaquelle.	
Temperature	12° C				13° C.	
PROPERTIES.						
Primary salinity	80.4		66.4		80.2	
Secondary salinity	16.0		17.4		18.4	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	3.6		16.2		1.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	96.2		71.2		98.4	
Sulphate salinity			11.2			
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	3 .2	180.3	32.1	0.7582	39.2	178.0
Potassium (K)	.5	2.043	1.1	.0262	.4	1.918
Lithium (Li)	.4	1.542			.4	1.543
Ammonium (NH_4)	.1	.4185			.1	.4187
Alkalies	40.2		33.2		40.1	
Calcium (Ca)	8.3	38.15	5.3	.1280	8.1	36.67
Magnesium (Mg)	1.2	5.635	11.1	.2748	1.4	6.55
Barium (Ba)	.1	.6205			.2	.8559
Strontium (Sr)	.2	1.004			.2	1.062
Earths	9.8		[a] 16.8		9.9	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)				.0		
Cobalt (Co)				.0		
Copper (Cu)				.0		
Cadmium (Cd)						
Lead (Pb)				.0		
Zinc (Zn)	.0	.1123	[a] .4	.0098	.0	.0044
Metals						
Sum of bases	50.0	229.8	50.0	1.197	50.0	227.02
Sulphate (SO_4)			5.6	.1346		
Chloride (Cl)	48.1	221.0	35.6	.8531	49.2	223.1
Bromide (Br)	.1	.4844		Trace.	.1	.5722
Iodide (I)	.0	.0029			.0	.0026
Fluoride (F)						
Nitrate (NO_3)			.7	.0173		
Thiosulphate (S_2O_3)						
Strong acids	48.2		41.9		49.3	
Carbonate (CO_3)			8.0	.1903	.7	3.336
Sulphide (S)	1.8	8.323				
Hydroxyl (OH)						
Arsenate (AsO_4)	.0	.0041			.0	.0038
Phosphate (PO_4)	.0	.0071	.1	.0017	.0	.0074
Weak acids	1.8		8.1		.7	
Sum of acids	50.0	229.8	50.0	1.197	50.0	227.02
Total value of reacting solids	100.0	459.6	100.0	2.394	100.0	454.0
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	13,562		74		13,274	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	37		3		35	
Total dissolved solids	13,599		77		13,309	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	123		3		260	

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[a] The reacting value of the zinc is included with that of the earths.

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	52		54		57	
Source of water	Sea water		Grossherzogin-Karolinenquelle.		Antonienquelle.	
Temperature			14° C		28° C.	
PROPERTIES.						
Primary salinity	78.6		75.4		61.6	
Secondary salinity	20.8		22.0			
Tertiary salinity						
Primary alkalinity					21.8	
Secondary alkalinity	.6		2.6		16.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	90.0		75.2		18.2	
Sulphate salinity	9.2		22.2		43.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	38.5	466.4	37.5	165.1	40.4	7.454
Potassium (K)	.8	9.779	.2	.9469	1.2	.2248
Lithium (Li)			.0	.0733	.1	.02479
Ammonium (NH_4)			.0	.0448		
Alkalies	39.3		37.7		41.7	
Calcium (Ca)	1.7	20.96	10.1	44.67	6.8	1.255
Magnesium (Mg)	9.0	108.2	2.1	9.095	1.4	.2553
Barium (Ba)						Trace.
Strontium (Sr)			.1	.2873	.1	.009325
Earths	10.7		12.3		8.3	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						Trace.
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						Trace.
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)				Trace.		Trace.
Metals						
Sum of bases	50.0	605.3	50.0	220.2	50.0	9.223
Sulphate (SO_4)	4.6	56.13	11.1	49.03	21.7	3.993
Chloride (Cl)	45.0	544.9	37.6	165.4	9.1	1.681
Bromide (Br)	.1	.8257	.0	.0461	.0	.0028
Iodide (I)			.0	.0001	.0	.00004
Fluoride (F)						Trace.
Nitrate (NO_3)				Trace.		
Thiosulphate (S_2O_3)						
Strong acids	49.7		48.7		30.8	
Carbonate (CO_3)	.3	3.484	1.3	5.740	18.1	3.347
Sulphide (S)						
Hydroxyl (OH)					1.1	.191
Arsenate (AsO_4)					.0	.0021
Phosphate (PO_4)			.0	.0004	.0	.0054
Weak acids	.3		1.3		19.2	
Sum of acids	50.0	605.3	50.0	220.2	50.0	9.223
Total value of reacting solids	100.0	121.1	100.0	440.4	100.0	18.446
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	35,139		13,436		635	
Colloids (SO_2, All_2O_3, Fe_2O_3, BO_2, etc.)			21		76	
Total dissolved solids	35,139		13,457		711	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)			46		0	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	58		59		61	
Source of water	Carlsbad Sprudel.		Néris-les-Bains		Lullusquelle.	
Temperature	166° F		50°-52.8°C		10.5° C.	
PROPERTIES.						
Primary salinity	60.0		51.8		69.2	
Secondary salinity					13.4	
Tertiary salinity						
Primary alkalinity	28.2		35.6			
Secondary alkalinity	11.8		12.6		17.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	20.4		18.2		16.4	
Sulphate salinity	39.6		33.6		66.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million*
Sodium (Na)	43.4	76.39	42.0	14.27	34.2	41.67
Potassium (K)	.6	1.079	1.6	.5312	.4	.4293
Lithium (Li)	.1	.1667	.1	.02728	.0	.0351
Ammonium (NH_4)				Trace.		
Alkalies	44.1		43.7		34.6	
Calcium (Ca)	3.7	6.438	5.7	1.945	12.7	15.41
Magnesium (Mg)	2.2	3.909	.6	.2160	2.5	3.09
Barium (Ba)				Trace.		
Strontium (Sr)					.1	.1484
Earths	5.9		6.3		[a] 15.4	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				Trace.		
Cadmium (Cd)						
Lead (Pb)				Trace.		
Zinc (Zn)		Trace.			[a] .1	.1316
Metals						
Sum of bases	50.0	87.99	50.0	16.99	50.0	60.91
Sulphate (SO_4)	19.8	34.83	16.8	5.694	33.0	40.26
Chloride (Cl)	10.1	17.80	9.1	3.102	8.2	9.964
Bromide (Br)		Trace.			.0	.0017
Iodide (I)		Trace.		Trace.	.0	.00002
Fluoride (F)	.1	.08777		Trace.		
Nitrate (NO_3)					.1	.0607
Thiosulphate (S_2O_3)						
Strong acids	30.0		25.9		41.3	
Carbonate (CO_3)	20.0	35.26	24.1	8.194	8.7	10.63
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)		Trace.			.0	.0006
Phosphate (PO_4)	.0	.01354			.0	.0004
Weak acids	20.0		24.1		8.7	
Sum of acids	50.0	87.99	50.0	16.99	50.0	60.91
Total value of reacting solids	100.0	176.08	100.0	33.98	100.0	121.8
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	6,434		1,274		4,274	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	74		109		94	
Total dissolved solids	6,508		1,383		4,368	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	190		45		10	

[a] The reacting value of the zinc is included with that of the earths.

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	62		63		85	
Source of water	Carolaquelle		Fontinalissprudel		Höllensprudel.	
Temperature	16.9° C		14.7° C		14.5° C.	
PROPERTIES.						
Primary salinity	37.8		6.0		1.2	
Secondary salinity	24.6					
Tertiary salinity						
Primary alkalinity			30.6		2.2	
Secondary alkalinity	37.6		63.4		96.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	15.6		4.4		.4	
Sulphate salinity	46.6		1.6		.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	17.3	10.34	17.4	12.23	1.6	0.4888
Potassium (K)	1.4	.8083	.8	.5427	.1	.0372
Lithium (Li)	.2	.1	.1	.0704	.0	.0022
Ammonium (NH_4)		Trace.	.0	.0251		
Alkalies	18.9		18.3		1.7	
Calcium (Ca)	24.4	14.55	9.8	6.866	39.2	11.76
Magnesium (Mg)	6.6	3.935	21.9	15.39	9.1	2.737
Barium (Ba)			.0	.0014		
Strontium (Sr)	.1	.0599				
Earths	31.1		31.7		48.3	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)					.0	.001
Cobalt (Co)					.0	.0003
Copper (Cu)						Trace.
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)	.0	.0154	.0	.0045	.0	.0013
Metals						
Sum of bases	50.0	29.81	50.0	35.13	50.0	15.03
Sulphate (SO_4)	23.3	13.89	.8	.5452	.3	.096
Chloride (Cl)	7.8	4.668	2.2	1.547	.2	.0597
Bromide (Br)	.0	.0029	.0	.002		
Iodide (I)	.0	.00002	.0	.00001	.0	.000003
Fluoride (F)						
Nitrate (NO_3)	.1	.0628	.0	.0191	.1	.016
Thiosulphate (S_2O_3)						
Strong acids	31.2		3.0		.6	
Carbonate (CO_3)	18.8	11.19	47.0	33.01	49.4	14.85
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)			.0	.0004	.0	.0003
Phosphate (PO_4)		Trace.	.0	.0094	.0	.0019
Weak acids	18.8		47.0		49.4	
Sum of acids	50.0	29.81	50.0	35.13	50.0	15.03
Total value of reacting solids	100.0	59.62	100.0	70.26	100.0	30.06
BASE ANALYSIS.						
(Summary by weight, in parts per million.)						
Total weight of reacting solids	2,132		2,726		1,196	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	13		23		116	
Total dissolved solids	2,146		2,749		1,312	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	287		1,804		2,600	

TABLE 1.—*Chemical character and geochemical properties of foreign zinc-bearing and related waters*—Continued.

No. in synoptical table	94		97		113		119	
Source of water	Caspar-Heinrich-Quelle.		Eulenhöfer Quelle.		Cransac Spring		Guber Spring.	
Temperature	10.2° C		9.4° C		32°-48° C			
PROPERTIES.								
Primary salinity	2.4		6.8		5.0		2.6	
Secondary salinity	3.6		12.0		88.6		6.2	
Tertiary salinity					6.4		90.0	
Primary alkalinity								
Secondary alkalinity	94.0		81.2					
Tertiary alkalinity							1.2	
	100.0		100.0		100.0		100.0	
Chloride salinity	.8		4.4		.4		.2	
Sulphate salinity	5.2		14.4		99.6		98.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	0.8	0.3001	2.9	0.2446	1.2	1.557	0.4	0.09279
Potassium (K)	.4	.1390	.5	.0384	1.3	1.662	.9	.2177
Lithium (Li)		Trace.	.0	.0029		Trace.		
Ammonium (NH_4)								
Alkalies	1.2		3.4		2.5		1.3	
Calcium (Ca)	32.9	12.60	30.4	2.588	18.1	22.94	1.4	.3518
Magnesium (Mg)	15.9	6.102	16.2	1.384	26.2	33.23	1.7	.4173
Barium (Ba)	.0	.0021	.0	.0011				
Strontium (Sr)	.0	.0118		Trace.				
Earths	48.8		46.6		44.3		3.1	
Iron (Fe)							22.8	5.622
Aluminum (Al)					2.4	3.084	18.4	4.538
Manganese (Mn)					.8	1.061		
Hydrogen (H)								
Nickel (Ni)			.0	.0008	.0	.007890		
Cobalt (Co)								
Copper (Cu)				Trace.				
Cadmium (Cd)								
Lead (Pb)				Trace.			3.3	.8300
Zinc (Zn)		Trace.	.0	.0009		Trace.	1.1	.2792
Metals					3.2		45.6	
Sum of bases	50.0	19.16	50.0	4.261	50.0	63.54	50.0	12.35
Sulphate (SO_4)	2.6	1.012	7.2	.6105	49.8	63.26	49.3	14.18
Chloride (Cl)	.4	.1356	2.2	.1847	.2	.2751	.1	.03314
Bromide (Br)		Trace.	.0	.0006				
Iodide (I)		Trace.	.0	.00004				
Fluoride (F)								
Nitrate (NO_3)		Trace.						
Thiosulphate (S_2O_3)								
Strong acids	3.0		9.4		50.0		49.4	
Carbonate (CO_3)	47.0	18.00	40.2	3.425				
Sulphide (S)								
Hydroxyl (OH)								
Arsenate (AsO_4)			.0	.004			.6	.1362
Phosphate (PO_4)	.0	.0043	.4	.0364		Trace.		
Weak acids	47.0		40.6				.6	
Sum of acids	50.0	19.16	50.0	4.261	50.0	63.54	50.0	12.35
Total value of reacting solids	100.0	38.32	100.0	8.522	100.0	127.1	100.0	24.70
BASE ANALYSIS. (Summary by weight, in parts per million.)								
Total weight of reacting solids	1,492		323		4,060		775	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	23		25		87		7	
Total dissolved solids	1,515		348		4,147		782	
Gases:								
Hydrogen sulphide (H_2S)	Trace.							
Carbon dioxide (CO_2)	1,868		119		18			

TABLE 2.—*Chemical character and geochemical properties of zinc-bearing and related waters in Eastern, Central, and Southern States.*

No. in synoptical table	8		28		66	
Source of water	Thompson Spring		Caddo oil well		Minnequa Spring.	
Temperature					47° F.	
PROPERTIES.						
Primary salinity	30.0		91.4		2.8	
Secondary salinity			6.2			
Tertiary salinity						
Primary alkalinity	25.8				13.8	
Secondary alkalinity	44.2		2.4		83.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	18.6		77.8		2.6	
Sulphate salinity	10.8		19.8		.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	20.8	0.5339	41.3	191.4	7.7	0.3276
Potassium (K)	6.6	.1700	4.4	20.48	.6	.02385
Lithium (Li)	.5	.01404				Trace.
Ammonium (NH_4)					.0	.00005
Alkalies	27.9		45.7		8.3	
Calcium (Ca)	12.4	.3186	4.3	19.96	32.4	1.385
Magnesium (Mg)	9.7	.2491		Trace.	9.2	.3921
Barium (Ba)					.0	.00208
Strontium (Sr)						
Earths	22.1		4.3		[a] 41.7	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.				
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.			[b] .1	.00311
Metals						
Sum of bases	50.0	1.286	50.0	231.8	50.0	2.134
Sulphate (SO_4)	5.4	.1397	9.9	45.80	.1	.00511
Chloride (Cl)	9.3	.2385	38.9	180.5	1.3	.05619
Bromide (Br)	.3	.06676				
Iodide (I)		Trace.				
Fluoride (F)		Trace.				
Nitrate (NO_3)					.0	.00005
Thiosulphate (S_2O_3)						
Strong acids	15.0		48.8		1.4	
Carbonate (CO_3)	35.0	.9007	1.2	5.556	47.9	2.043
Sulphide (S)						
Hydroxyl (OH)					.6	.02476
Arsenate (AsO_4)		Trace.				
Phosphate (PO_4)					.1	.00407
Weak acids	35.0		1.2		48.6	
Sum of acids	50.0	1.286	50.0	231.8	50.0	2.134
Total value of reacting solids	100.0	2.572	100.0	463.6	100.0	4.268
BASE ANALYSIS. (Summary by weight in parts per million.)						
Total weight of reacting solids	99		14,539		169	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	21		0		14	
Total dissolved solids	120		14,539		183	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)						

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[a] The reacting values of the metals is included with that of the earths.
[b] The reacting value of the zinc is included with that of the earths.

TABLE 2.—*Chemical character and geochemical properties of zinc-bearing and related waters in Eastern, Central, and Southern States*—Continued.

No. in synoptical table	67		73		93	
Source of water	Mida Spring		Coppahaunk Spring.		Roanoke Red Sulphur Springs.	
Temperature	60° F				53°-60° F.	
PROPERTIES.						
Primary salinity	10.2		6.6		14.0	
Secondary salinity			.2		13.8	
Tertiary salinity						
Primary alkalinity	13.8					
Secondary alkalinity	76.0		93.2		72.2	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	3.4		6.2		1.4	
Sulphate salinity	3.2		.6		26.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	11.7	0.4102	2.3	0.2349	6.3	0.8042
Potassium (K)	.3	.01023	.7	.07424	.5	.06488
Lithium (Li)	.0	.00126	.3	.02738	.1	.00993
Ammonium (NH_4)					.1	.01712
Alkalies	12.0		3.3		7.0	
Calcium (Ca)	25.0	.8782	45.5	4.641	22.0	2.798
Magnesium (Mg)	13.0	.4573	1.2	.1233	18.5	2.343
Barium (Ba)		Trace.	.0	.00218		Trace
Strontium (Sr)			.0	.00228	2.5	.3184
Earths	38.0		46.7		43.0	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						Trace.
Cadmium (Cd)						
Lead (Pb)						Trace.
Zinc (Zn)		Trace.		Trace.		
Metals						
Sum of bases	50.0	1.757	50.0	5.105	50.0	6.356
Sulphate (SO_4)	1.6	.05596	.3	.03331	13.1	1.665
Chloride (Cl)	1.7	.06117	3.1	.3102	.7	.08593
Bromide (Br)				Trace.		
Iodide (I)				Trace.		
Fluoride (F)						
Nitrate (NO_3)	1.8	.06342			.1	.01078
Thiosulphate (S_2O_3)						
Strong acids	5.1		3.4		13.9	
Carbonate (CO_3)	44.5	1.562	46.6	4.757	36.1	4.594
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)			.0	.00073		Trace.
Phosphate (PO_4)	.4	.01491	.0	.00379		Trace.
Weak acids	44.9		46.6		36.1	
Sum of acids	50.0	1.757	50.0	5.105	50.0	6.356
Total value of reacting solids	100.0	3.514	100.0	10.21	100.0	12.712
BASE ANALYSIS.						
(Summary by weight, in parts per million.)						
Total weight of reacting solids	138		415		484	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	59		43		15	
Total dissolved solids	197		458		499	
Gases:						
Hydrogen sulphide (H_2S)					16	
Carbon dioxide (CO_2)					106	

Table 2.—*Chemical character and geochemical properties of zinc-bearing and related waters in Eastern, Central, and Southern States*—Continued.

No. in synoptical table	106		107		112	
Source of water	Johnson well		Kings Mineral Spring.		Allegheny Spring.	
Temperature					56° F.	
PROPERTIES.						
Primary salinity	33.6		38.6		2.8	
Secondary salinity	57.2		58.6		94.2	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	9.2		2.8		3.0	
Tertiary alkalinity						
	100.0		200.0		100.0	
Chloride salinity	56.0		19.6		.2	
Sulphate salinity	34.6		77.6		95.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	16.5	10.74	18.9	94.73	0.5	0.4976
Potassium (K)	.3	.2171	.4	1.953	.8	.7281
Lithium (Li)				Trace.		Trace.
Ammonium (NH_4)					.1	.1197
Alkalies	16.8		19.3		.4	
Calcium (Ca)	28.8	18.84	4.5	22.77	32.2	30.23
Magnesium (Mg)	4.4	2.892	26.2	131.5	16.4	15.37
Barium (Ba)				Trace.	.0	.00347
Strontium (Sr)				Trace.	.0	.0139
Earths	33.2		30.7		48.6	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)				Trace.		
Cobalt (Co)						Trace.
Copper (Cu)						Trace.
Cadmium (Cd)						
Lead (Pb)						Trace.
Zinc (Zn)		Trace.		Trace.		Trace.
Metals						
Sum of bases	50.0	32.69	50.0	250.9	50.0	46.96
Sulphate (SO_4)	17.3	11.30	38.8	194.9	47.5	44.60
Chloride (Cl)	28.0	18.33	9.8	49.07	.1	.08192
Bromide (Br)				Trace.		
Iodide (I)						
Fluoride (F)					.0	.00877
Nitrate (NO_3)					.9	.8497
Thiosulphate (S_2O_3)	.1	.04413				
Strong acids	45.4		48.6		48.5	
Carbonate (CO_3)	4.6	3.02	1.4	6.983	1.5	1.41
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)				Trace.	.0	.01362
Weak acids	4.6		1.4		1.5	
Sum of acids	50.0	32.69	50.0	250.9	50.0	46.84
Total value of reacting solids	100.0	65.38	100.0	501.8	100.0	93.68
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	2,048		15,836		3,121	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	56		11		22	
Total dissolved solids	2,104		15,847		3,143	
Gases:						
Hydrogen sulphide (H_2S)					Trace.	
Carbon dioxide (CO_2)	66				39	

Table 2.—*Chemical character and geochemical properties of zinc-bearing and related waters in Eastern, Central, and Southern States*—Continued.

No. in synoptical table	117		118	
Source of water	Bedford Alum Spring.		Rockbridge Alum Spring No. 2.	
Temperature	56° F.		50°–56° F.	
PROPERTIES.				
Primary salinity	3.2		.6	
Secondary salinity	28.0		14.2	
Tertiary salinity	68.8		85.2	
Primary alkalinity	....		....	
Secondary alkalinity	....		....	
Tertiary alkalinity	....		....	
	100.0		100.0	
Chloride salinity	.4		.2	
Sulphate salinity	99.0		99.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	0.8	0.2681	0.1	0.03954
Potassium (K)	.4	.1402	.2	.08063
Lithium (Li)	.2	.07446	.0	.00616
Ammonium (NH_4)	.2	.05118	....	Trace.
Alkalies	1.6	....	.3	....
Calcium (Ca)	3.8	1.356	2.5	.8693
Magnesium (Mg)	10.2	3.633	4.6	1.597
Barium (Ba)	....	....	....	....
Strontium (Sr)	....	....	....	....
Earths	14.0	....	7.1	....
Iron (Fe)	9.7	3.438	1.0	.3346
Aluminum (Al)	20.3	7.240	37.1	12.76
Manganese (Mn)	.1	.04314	.1	.02037
Hydrogen (H)	3.9	1.396	4.0	1.358
Nickel (Ni)	.0	.00887	.1	.03098
Cobalt (Co)	.0	.01545	.0	.00445
Copper (Cu)	.4	.1292	.1	.02157
Cadmium (Cd)	....	....	....	....
Lead (Pb)	....	....	....	Trace.
Zinc (Zn)	.0	.01466	.2	.08165
Metals	34.4	....	42.6	....
Sum of bases	50.0	17.81	50.0	17.20
Sulphate (SO_4)	49.5	17.64	49.9	17.17
Chloride (Cl)	.2	.05786	.1	.03218
Bromide (Br)	....	....	....	....
Iodide (I)	....	....	....	....
Fluoride (F)	....	Trace.	....	Trace.
Nitrate (NO_3)	.3	.1113	....	....
Thiosulphate (S_2O_3)	....	....	....	....
Strong acids	50.0	....	50.0	....
Carbonate (CO_3)	....	....	....	....
Sulphide (S)	....	....	....	....
Hydroxyl (OH)	....	....	....	....
Arsenate (AsO_4)	....	....	....	Trace.
Phosphate (PO_4)	....	Trace.	....	Trace.
Weak acids	....	....	....	....
Sum of acids	50.0	17.81	50.0	17.20
Total value of reacting solids	100.0	35.62	100.0	34.40
BASE ANALYSIS. (Summary by weight, in parts per million.)				
Total weight of reacting solids	1,185		1,002	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	29		63	
Total dissolved solids	1,214		1,065	
Gases:				
Hydrogen sulphide (H_2S)	....		....	
Carbon dioxide (CO_2)	119		93	

Table 3.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kentucky.*

No. in synoptical table	19		21		22	
Source of water	Renfro well		Sanders well		Sadieville well.	
PROPERTIES.						
Primary salinity	55.6		65.6		66.6	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	10.2		7.4		5.0	
Secondary alkalinity	34.2		27.0		28.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	57.4		36.0		65.6	
Sulphate salinity	8.2		29.6		1.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	31.9	7.160	34.6	15.05	35.8	12.18
Potassium (K)	1.0	.2173	1.7	.7565		
Lithium (Li)	.0	.006768	.2	.07309		Trace.
Ammonium (NH_4)						
Alkalies	32.9		36.5		35.8	
Calcium (Ca)	7.5	1.689	6.7	2.895	7.0	2.395
Magnesium (Mg)	9.5	2.139	6.2	2.721	7.2	2.466
Barium (Ba)						
Strontium (Sr)	.1	.01353	.6	.2479		
Earths	17.1		13.5		14.2	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.		Trace.		Trace.
Metals						
Sum of bases	50.0	11.23	50.0	21.74	50.0	17.041
Sulphate (SO_4)	4.1	.9132	14.8	6.448	.5	.1853
Chloride (Cl)	23.7	5.328	18.0	7.840	32.8	11.17
Bromide (Br)				Trace.		
Iodide (I)				Trace.		
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	27.8		32.8		33.3	
Carbonate (CO_3)	22.2	4.989	16.3	7.075	16.7	5.6857
Sulphide (S)						
Hydroxyl (OH)			.9	.3771		
Arsenate (AsO_4)						
Phosphate (PO_4)				Trace.		
Weak acids	22.2		17.2		16.7	
Sum of acids	50.0	11.23	50.0	21.74	50.0	17.04
Total value of reacting solids	100.0	22.46	100.0	43.48	100.0	34.08
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	772		1,514		1,110	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	8		4		10	
Total dissolved solids	780		1,518		1,120	
Gases:						
Hydrogen sulphide (H_2S	9		22			
Carbon dioxide (CO_2)						

TABLE 3.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kentucky*—Continued.

No. in synoptical table	24		36		48	
Source of water	Hopkinsville well		Estill well		Sharp well.	
PROPERTIES.						
Primary salinity	79.2		86.0		80.2	
Secondary salinity			10.6		17.6	
Tertiary salinity						
Primary alkalinity	.4					
Secondary alkalinity	20.4		3.4		2.2	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	60.6		96.4		95.4	
Sulphate salinity	18.6		.2		2.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	39.5	42.24	43.0	74.17	39.5	227.3
Potassium (K)	.2	.2388			.6	3.203
Lithium (Li)	.1	.0802				Trace.
Ammonium (NH_4)						
Alkalies	39.8		43.0		40.1	
Calcium (Ca)	3.0	3.205	3.3	5.689	5.1	29.487
Magnesium (Mg)	6.9	7.425	3.7	6.412	4.8	27.77
Barium (Ba)						
Strontium (Sr)	.3	.3144				Trace.
Earths	10.2		7.0		9.9	
Iron (Fe)						
Aluminum Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.		Trace.		Trace.
Metals						
Sum of bases	50.0	53.50	50.0	86.271	50.0	287.8.
Sulphate (SO_4)	9.3	9.953	.1	.2290	1.2	6.841
Chloride (Cl)	30.3	32.46	48.2	83.19	47.7	274.3
Bromide (Br)						Trace.
Iodide (I)						Trace.
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	39.6		48.3		48.9	
Carbonate (CO_3)	3.0	3.232	1.7	2.852	.8	4.873
Sulphide (S)	7.4	7.858			.3	1.793
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	10.4		1.7		1.1	
Sum of acids	50.0	53.50	50.0	86.27	50.0	287.89
Total value of reacting solids	100.0	107.0	100.0	172.5	100.0	575.6
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	3,116		5,032		16,672	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	11		12		7	
Total dissolved solids	3,127		5,044		16,679	
Gases:						
Hydrogen sulphide (H_2S)	63		Present.		15	
Carbon dioxide (CO_2)						

Table 3.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kentucky*—Continued.

No. in synoptical table	49		53		65	
Source of water	Felix well		School well		Wilson well.	
PROPERTIES.						
Primary salinity	70.2		71.6		24.8	
Secondary salinity	18.4		22.0			
Tertiary salinity						
Primary alkalinity					20.2	
Secondary alkalinity	11.4		6.4		55.0	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	87.0		76.2		15.0	
Sulphate salinity	1.6		17.4		9.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na) Potassium (K)	35.1	18.31	35.5 .3	249.7 2.203	22.5	2.654
Lithium (Li)		Trace.		Trace.		Trace.
Ammonium (NH_4)						
Alkalies	35.1		35.8		22.5	
Calcium (Ca)	7.8	4.042	6.2	43.13	13.6	1.597
Magnesium (Mg)	7.1	3.699	8.0	56.41	13.9	1.644
Barium (Ba)						
Strontium (Sr)		Trace.		Trace.		
Earths	14.9		14.2		27.5	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.		Trace.		Trace.
Metals						
Sum of bases	50.0	26.05	50.0	351.4	50.0	5.895
Sulphate (SO_4)	.8	.4368	8.7	60.77	4.9	.5824
Chloride (Cl)	43.5	22.64	38.1	268.1	7.5	.8742
Bromide (Br)				Trace.		
Iodide (I)				Trace.		
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	44.3		46.8		12.4	
Carbonate (CO_3)	5.7	2.973			37.6	4.438
Sulphide (S)			3.2	22.56		
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)				Trace.		
Weak acids	5.7		3.2		37.6	
Sum of acids	50.0	26.05	50.0	351.4	50.0	5.895
Total value of reacting solids	100.0	52.10	100.0	702.8	100.0	11.79
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	1,552		20,158		443	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	33		9		10	
Total dissolved solids	1,585		20,167		453	
Gases:						
Hydrogen sulphide (H_2S)	Present.				Present.	
Carbon dioxide (CO_2)						

TABLE 3.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kentucky*—Continued.

No. in synoptical table	74		75		83	
Source of water	Louisville spring.		Sayre well		Royal Magnesian Spring.	
PROPERTIES.						
Primary salinity	3.6		3.8		3.6	
Secondary salinity	1.0		1.8			
Tertiary salinity						
Primary alkalinity					3.8	
Secondary alkalinity	95.4		94.4		92.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	2.4		3.8		1.2	
Sulphate salinity	1.2		1.8		6.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	1.4	0.1636	1.9	0.1914	0.6	0.05989
Potassium (K)	.4	.04713			1.2	.1194
Lithium (Li)		Trace.		Trace.		Trace.
Ammonium (NH_4)						
Alkalies	1.8		1.9		1.8	
Calcium (Ca)	23.5	2.732	41.7	4.291	24.4	2.406
Magnesium (Mg)	24.7	2.860	5.3	.5507	23.7	2.327
Barium (Ba)						
Strontium (Sr)		Trace.		Trace.		Trace.
Earths	48.2		[a] 48.1		[a] 48.2	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.	[a] 1.1	.1101	[a] .1	.007975
Metals						
Sum of bases	50.0	5.803	50.0	5.143	50.0	4.920
Sulphate (SO_4)	.6	.07516	.9	.09577	3.1	.3021
Chloride (Cl)	1.2	.1350	1.9	.1889	.6	.05989
Bromide (Br)		Trace.				
Iodide (I)		Trace.				
Fluoride (F)						
Nitrate (NO_3)	.5	.05637				
Thiosulphate(S_2O_3)						
Strong acids	2.3		2.8		3.7	
Carbonate (CO_3)	47.7	5.536	47.2	4.859	46.3	4.5579
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	47.7		47.2		46.3	
Sum of acids	50.0	5.803	50.0	5.143	50.0	4.920
Total value of reacting solids	100.0	11.61	100.0	10.29	100.0	9.840
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	445		408		377	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	23		8		8	
Total dissolved solids	468		416		385	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)						

[a] The reacting value of the zinc is included with that of the earths.

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri.*

No. in synoptical table	27		32		38	
Source of water	Nevada well		Clinton well No. 2.		Silver well (to 1,100 feet).	
PROPERTIES.						
Primary salinity	66.6		58.6		75.0	
Secondary salinity	5.6		8.4		12.0	
Tertiary salinity	......		......		......	
Primary alkalinity	27.8		33.0		13.0	
Secondary alkalinity	......		......		......	
Tertiary alkalinity	......		......		......	
	100.0		100.0		100.0	
Chloride salinity	66.8		55.8		75.0	
Sulphate salinity	5.4		11.2		12.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	33.3	13.34	26.1	8.872	32.2	26.94
Potassium (K)	......	......	3.2	1.085	5.3	4.406
Lithium (Li)	......	......	......	......	......	......
Ammonium (NH_4)	......	......	......	......	......	......
Alkalies	33.3	......	29.3	......	37.5	......
Calcium (Ca)	10.0	3.994	11.8	4.012	6.9	5.743
Magnesium (Mg)	6.7	2.678	8.9	3.001	5.6	4.651
Barium (Ba)	......	......	......	......	......	......
Strontium (Sr)	......	......	......	......	......	......
Earths	16.7	......	20.7	......	12.5	......
Iron (Fe)	......	......	......	......	......	......
Aluminum (Al)	......	......	......	......	......	......
Manganese (Mn)	......	......	......	......	......	......
Hydrogen (H)	......	......	......	......	......	......
Nickel (Ni)	......	......	......	......	......	......
Cobalt (Co)	......	......	......	......	......	......
Copper (Cu)	......	......	......	Trace.	......	......
Cadmium (Cd)	......	......	......	......	......	......
Lead (Pb)	......	......	......	Trace.	......	......
Zinc (Zn)	......	......	......	Trace.	......	......
Metals	......	......	......	......	......	......
Sum of bases	50.0	20.01	50.0	16.97	50.0	41.74
Sulphate (SO_4)	2.7	1.099	5.6	1.906	6.0	4.982
Chloride (Cl)	33.4	13.36	27.9	9.478	37.5	31.34
Bromide (Br)	......	......	......	......	......	......
Iodide (I)	......	......	......	......	......	......
Fluoride (F)	......	......	......	......	......	......
Nitrate (NO_3)	......	......	......	......	......	......
Thiosulphate (S_2O_3)	......	......	......	......	......	......
Strong acids	36.1	......	33.5	......	43.5	......
Carbonate (CO_3)	13.9	5.557	16.5	5.585	6.5	5.42
Sulphide (S)	......	......	......	......	......	......
Hydroxyl (OH)	......	......	......	......	......	......
Arsenate (AsO_4)	......	......	......	......	......	......
Phosphate (PO_4)	......	......	......	......	......	......
Weak acids	13.9	......	16.5	......	6.5	......
Sum of acids	50.0	20.01	50.0	16.97	50.0	41.74
Total value of reacting solids	100.0	40.02	100.0	33.94	100.0	83.48
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	1,285		1,132		2,651	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	14		4		9	
Total dissolved solids	1,299		1,136		2,660	
Gases:						
Hydrogen sulphide (H_2S)	......		1		......	
Carbon dioxide (CO_2)	......		......		......	

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	40		42		51	
Source of water	Clinton well No. 3 (Britts).		Clinton well No. 1.		Brunswick well.	
PROPERTIES.						
Primary salinity	62.4		65.0		76.2	
Secondary salinity	12.4		13.8		20.4	
Tertiary salinity						
Primary alkalinity	25.2		21.2		3.4	
Secondary alkalinity						
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	66.8		70.8		86.4	
Sulphate salinity	8.0		8.0		10.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	30.2	14.31	31.8	18.23	38.1	204.5
Potassium (K)	1.0	.4777	.7	.4246		
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	31.2		32.5		38.1	
Calcium (Ca)	11.1	5.278	10.2	5.823	6.9	36.90
Magnesium (Mg)	7.7	3.646	7.3	4.181	5.0	27.05
Barium (Ba)						
Strontium (Sr)						
Earths	18.8		17.5		11.9	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.		Trace.		
Cadmium (Cd)						
Lead (Pb)		Trace.		Trace.		
Zinc (Zn)		Trace.		Trace.		
Metals						
Sum of bases	50.0	23.71	50.0	28.66	50.0	268.5
Sulphate (SO_4)	4.0	1.886	4.0	2.296	5.1	27.15
Chloride (Cl)	33.4	15.83	35.4	20.29	43.2	232.0
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	37.4		39.4		48.3	
Carbonate (CO_3)	12.6	5.988	10.6	6.073	1.7	9.302
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	12.6		10.6		1.7	
Sum of acids	50.0	23.71	50.0	28.66	50.0	268.5
Total value of reacting solids	100.0	47.42	100.0	57.32	100.0	537.0
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	1,538		1,804		15,875	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	14		11		5	
Total dissolved solids	1,552		1,815		15,880	
Gases:						
Hydrogen sulphide (H_2S)			4		Present.	
Carbon dioxide (CO_2)						

TABLE 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	55		56		64	
Source of water	Silver well (below 1,100 feet).		Belcher well		Cornfield well.	
Temperature			23° C.=73.4 F.			
PROPERTIES.						
Primary salinity	76.0		73.4		3.8	
Secondary salinity	23.4		23.6			
Tertiary salinity					20.6	
Primary alkalinity	.6		3.0		75.6	
Secondary alkalinity						
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	91.4		89.0		3.2	
Sulphate salinity	8.0		8.0		.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	30.8	74.47	36.0	107.5	12.2	1.048
Potassium (K)	7.2	17.34	.7	2.150		
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	38.0		36.7		12.2	
Calcium (Ca)	4.0	9.825	8.3	24.70	30.9	2.657
Magnesium (Mg)	8.0	19.28	5.0	14.80	6.9	.5952
Barium (Ba)						
Strontium (Sr)						
Earths	12.0		13.3		37.8	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)						
Metals						
Sum of bases	50.0	120.9	50.0	149.2	50.0	4.300
Sulphate (SO_4)	4.0	9.683	4.0	11.98	.3	.02498
Chloride (Cl)	45.7	110.6	44.5	132.7	1.6	.1410
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	49.7		48.5		1.9	
Carbonate (CO_3)	.3	.6150	1.5	4.489	48.1	4.134
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	.3		1.5		48.1	
Sum of acids	50.0	120.9	50.0	149.2	50.0	4.300
Total value of reacting solids	100.0	241.8	100.0	298.4	100.0	8.600
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	7,245		8,787		931	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	9		9		11	
Total dissolved solids	7,254		8,796		942	
Gases:						
Hydrogen sulphide (H_2S)			14			
Carbon dioxide (CO_2)			55			

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	68		76		82	
Source of water	Missouri Lead & Zinc Co.'s well (at 1,387 feet).		Oronogo well.		Missouri Lead & Zinc Co.'s well (at 940 feet).	
PROPERTIES.						
Primary salinity	15.0		10.2		11.6	
Secondary salinity			2.2			
Tertiary salinity	8.6				8.2	
Primary alkalinity	76.4		87.6		80.2	
Secondary alkalinity						
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	8.0		10.2		5.6	
Sulphate salinity	7.0		2.2		6.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	11.8	1.007	5.1	0.3601	9.9	0.9836
Potassium (K)						
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	11.8		5.1		9.9	
Calcium (Ca)	21.7	1.844	27.7	1.963	22.1	2.196
Magnesium (Mg)	16.5	1.405	17.2	1.220	18.0	1.781
Barium (Ba)						
Strontium (Sr)						
Earths	38.2		44.9		40.1	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)						
Metals						
Sum of bases	50.0	4.256	50.0	3.543	50.0	4.961
Sulphate (SO_4)	3.5	.2989	1.1	.0775	3.0	.2994
Chloride (Cl)	4.0	.3374	5.1	.3590	2.8	.2814
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	7.5		6.2		5.8	
Carbonate (CO_3)	42.5	3.620	43.8	3.107	44.2	4.380
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	42.5		43.8		44.2	
Sum of acids	50.0	4.256	50.0	3.543	50.0	4.961
Total value of reacting solids	100.0	8.512	100.0	7.086	100.0	9.922
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	324		268		380	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	12		13		16	
Total dissolved solids	336		281		396	
Gases:						
Hydrogen sulphide (H_2S)	Present.					
Carbon dioxide (CO_2)						

TABLE 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	84		86		87	
Source of water	Freeman Foundry well.		Fulton Hospital well.		Cox Spring.	
Temperature	65° F					
PROPERTIES.						
Primary salinity	18.2		28.8		5.2	
Secondary salinity					.4	
Tertiary salinity	3.4		2.0			
Primary alkalinity	78.4		69.2		94.4	
Secondary alkalinity						
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	3.8		10.8		2.0	
Sulphate salinity	14.4		18.0		3.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	10.8	1.099	15.4	2.943	2.1	0.1044
Potassium (K)					.5	.02560
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	10.8		15.4		2.6	
Calcium (Ca)	26.0	2.633	18.0	3.420	43.2	2.126
Magnesium (Mg)	13.2	1.340	16.6	3.171	4.2	.2055
Barium (Ba)						
Strontium (Sr)						
Earths	39.2		34.6		47.4	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				Trace.		Trace.
Cadmium (Cd)						
Lead (Pb)						0
Zinc (Zn)				Trace.		0
Metals						
Sum of bases	50.0	5.072	50.0	9.534	50.0	2.462
Sulphate (SO_4)	7.2	.7248	9.0	1.711	1.8	.08744
Chloride (Cl)	1.9	.1970	5.4	1.025	1.0	.04794
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	9.1		14.4		2.8	
Carbonate (CO_3)	40.9	4.150	35.6	6.798	47.2	2.326
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	40.9		35.6		47.2	
Sum of acids	50.0	5.072	50.0	9.534	50.0	2.462
Total value of reacting solids	100.0	10.144	100.0	19.068	100.0	4.924
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	389		708		196	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	8		37		15	
Total dissolved solids	397		745		211	
Gases:						
Hydrogen sulphide (H_2S)					0	
Carbon dioxide (CO_2)					1	

TABLE 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	88		89		91	
Source of water	Harrington well		Providence well		Alba well.	
PROPERTIES.						
Primary salinity	10.6		7.2		6.6	
Secondary salinity	.6		3.8		5.0	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	88.8		89.0		88.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	4.4		1.4		3.8	
Sulphate salinity	6.8		9.6		7.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	5.1	0.3549	3.6	0.2652	2.9	0.2774
Potassium (K)	.2	.01274			.4	.04034
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	5.3		3.6		3.3	
Calcium (Ca)	25.2	1.747	27.1	1.992	41.2	3.940
Magnesium (Mg)	18.8	1.309	19.3	1.419	5.3	.5059
Barium (Ba)						
Strontium (Sr)						
Earths	[a] 44.7		46.4		[a] 46.7	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		.0		.0		.0
Cadmium (Cd)						
Lead (Pb)		.0	.0	.0002643		.0
Zinc (Zn)	[a] .7	.04894		.0	[a] .2	.02202
Metals						
Sum of bases	50.0	3.473	50.0	3.676	50.0	4.786
Sulphate (SO_4)	3.4	.2374	4.8	.3550	3.9	.3698
Chloride (Cl)	2.2	.1495	.7	.04786	1.9	.1833
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	5.6		5.5		5.8	
Carbonate (CO_3)	44.4	3.086	44.5	3.273	44.2	4.233
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	44.4		44.5		44.2	
Sum of acids	50.0	3.473	50.0	3.676	50.0	4.786
Total value of reacting solids	100.0	6.946	100.0	7.352	100.0	9.572
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	266		282		282	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	11		18		14	
Total dissolved solids	277		300		296	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)	12				5	

[a] The reacting value of the zinc is included with that of the earths.

TABLE 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	92		95		96	
Source of water	Redell well		Ash Grove well		Webb City well	
Temperature	66.5° F					
PROPERTIES.						
Primary salinity	15.6		3.4		4.2	
Secondary salinity	6.2		9.2		10.4	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	78.2		87.4		85.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	7.2		3.4		7.2	
Sulphate salinity	14.6		9.2		7.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	5.8	0.4176	1.7	0.1249	1.7	0.1104
Potassium (K)	2.0	.1434			.4	.02848
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	7.8		1.7		2.1	
Calcium (Ca)	27.7	2.011	26.8	1.954	28.2	1.893
Magnesium (Mg)	14.5	1.052	21.5	1.563	19.7	1.322
Barium (Ba)						
Strontium (Sr)						
Earths	42.2		48.3		47.9	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.				
Cadmium (Cd)						
Lead (Pb)		.0				
Zinc (Zn)		.0				
Metals						
Sum of bases	50.0	3.624	50.0	3.642	50.0	3.354
Sulphate (SO_4)	7.3	.5288	4.6	.3322	3.7	.2511
Chloride (Cl)	3.6	.2623	1.7	.1252	3.6	.2417
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	10.9		6.3		7.3	
Carbonate (CO_3)	39.1	2.833	43.7	3.185	42.7	2.861
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	39.1		43.7		42.7	
Sum of acids	50.0	3.624	50.0	3.642	50.0	3.354
Total value of reacting solids	100.0	7.248	100.0	7.284	100.0	6.708
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	276		275		253	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	48		10		10	
Total dissolved solids	324		285		263	
Gases:						
Hydrogen sulphide (H_2S)	0					
Carbon dioxide (CO_2)	0					

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	98		99		100	
Source of water	Freeman Foundry well.		Average of 10 mine waters in southeastern Missouri.		Winslow mine.	
PROPERTIES.						
Primary salinity	4.8		15.2		6.6	
Secondary salinity	12.2		17.6		23.0	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	83.0		67.2		70.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	4.4		13.0		1.2	
Sulphate salinity	12.6		19.8		28.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	2.4	0.1523	6.4	0.8739	2.4	0.2065
Potassium (K)			1.2	.1690	.9	.07855
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	2.4		7.6		3.3	
Calcium (Ca)	41.1	2.595	21.0	2.897	46.7	4.037
Magnesium (Mg)	6.5	.4110	21.4	2.954		
Barium (Ba)						
Strontium (Sr)						
Earths	47.6		42.4		46.7	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						.0
Lead (Pb)			.0	.00431		.0
Zinc (Zn)				.0		.0
Metals						
Sum of bases	50.0	3.158	50.0	6.898	50.0	.4.322
Sulphate (SO_4)	6.3	.3956	9.9	1.370	14.2	1.229
Chloride (Cl)	2.2	.1410	6.5	.8948	.6	.05358
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	8.5		16.4		14.8	
Carbonate (CO_3)	41.5	2.621	33.6	4.634	35.2	3.039
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	41.5		33.6		35.2	
Sum of acids	50.0	3.158	50.0	6.898	50.0	4.322
Total value of reacting solids	100.0	6.316	100.0	13.796	100.0	8.644
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	244		501		335	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	45		14		15	
Total dissolved solids	289		515		350	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)					9	

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	101		108		110	
Source of water	B. & C. mine		Sphalerite well		Lakeside Spring.	
PROPERTIES.						
Primary salinity	5.8		13.8		4.4	
Secondary salinity	34.2		44.6		64.4	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	60.0		41.6		31.2	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	1.2		6.8		3.6	
Sulphate salinity	38.8		51.6		65.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	2.7	0.4002	6.9	1.218	2.2	0.2684
Potassium (K)	.2	.03584				
Lithium (Li)		Trace.				
Ammonium (NH_4)						
Alkalies	2.9		6.9		2.2	
Caicium (Ca)	42.1	6.342	37.0	6.537	43.5	5.355
Magnesium (Mg)	4.7	.7151	6.1	1.069	4.3	.5341
Barium (Ba)						
Strontium (Sr)						
Earths	a 47.1		43.1		47.8	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.				
Cadmium (Cd)		.0				
Lead (Pb)		.0				
Zinc (Zn)	a .3	.03977				
Metals						
Sum of bases	50.0	7.533	50.0	8.824	50.0	6.157
Sulphate (SO_4)	19.4	2.931	25.8	4.555	32.6	4.017
Chloride (Cl)	.6	.08742	3.4	.5922	1.8	.2249
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	20.0		29.2		34.4	
Carbonate (CO_3)	30.0	4.514	20.8	3.677	15.6	1.915
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	30.0		20.8		15.6	
Sum of acids	50.0	7.533	50.0	8.824	50.0	6.157
Total value of reacting solids	100.0	15.066	100.0	17.648	100.0	12.314
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	567		536		438	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	15		32		10	
Total dissolved solids	582		568		448	
Gases:						
Hydrogen sulphide (H_2S)	0					
Carbon dioxide (CO_2)	2					

Table 4.—*Chemical character and geochemical properties of zinc-bearing and related waters in Missouri*—Continued.

No. in synoptical table	115		116	
Source of water	Missouri Zinc Fields.		Shoal Creek Spring.	
Temperature	64° F.			
PROPERTIES.				
Primary salinity	3.6		3.0	
Secondary salinity	56.4		45.2	
Tertiary salinity	31.8		32.6	
Primary alkalinity				
Secondary alkalinity				
Tertiary alkalinity	8.2		19.2	
	100.0		100.0	
Chloride salinity	.4		1.0	
Sulphate salinity	91.4		79.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	1.7	2.049	1.1	0.1566
Potassium (K)	.1	.1152	.4	.0640
Lithium (Li)				
Ammonium (NH_4)				
Alkalies	1.8		1.5	
Calcium (Ca)	24.4	29.73	20.5	3.049
Magnesium (Mg)	3.8	4.661	2.1	.3129
Barium (Ba)				
Strontium (Sr)				
Earths	28.2		22.6	
Iron (Fe)	7.9	9.634	.1	.02148
Aluminum (Al)	.8	.9299	.3	.04428
Manganese (Mn)	.1	.1165	.6	.08374
Hydrogen (H)				
Nickel (Ni)				
Cobalt (Co)				
Copper (Cu)		Trace.	.0	.00629
Cadmium (Cd)	.0	.01779	.1	.0089
Lead (Pb)		.0		Trace.
Zinc (Zn)	11.2	13.61	24.8	3.686
Metals	20.0		25.9	
Sum of bases	50.0	60.86	50.0	7.433
Sulphate (SO_4)	45.7	55.62	39.9	5.932
Chloride (Cl)	.2	.1861	.5	.07332
Bromide (Br)				
Iodide (I)				
Fluoride (F)				
Nitrate (NO_3)				
Thiosulphate (S_2O_3)				
Strong acids	45.9		40.4	
Carbonate (CO_3)	4.1	5.050	9.6	1.428
Sulphide (S)				
Hydroxyl (OH)				
Arsenate (AsO_4)				
Phosphate (PO_4)				
Weak acids	4.1		9.6	
Sum of acids	50.0	60.86	50.0	7.433
Total value of reacting solids	100.0	121.72	100.0	14.866
BASE ANALYSIS. (Summary by weight, in parts per million.)				
Total weight of reacting solids	4,417		570	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	36		14	
Total dissolved solids	4,453		584	
Gases:				
Hydrogen sulphide (H_2S)				
Carbon dioxide (CO_2)			43	

TABLE 5.—*Chemical character and geochemical properties of zinc-bearing and related waters in Arkansas.*

No. in synoptical table	35		72	
Source of water	White Sulphur Spring.		Black Sulphur Spring.	
Temperature			61.7° F.	
PROPERTIES.				
Primary salinity	55.2		43.2	
Secondary salinity	10.4			
Tertiary salinity				
Primary alkalinity				
Secondary alkalinity	34.4		56.8	
Tertiary alkalinity				
	100.0		100.0	
Chloride salinity	60.2		38.6	
Sulphate salinity	5.4		4.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	19.2	2.675	21.6	3.053
Potassium (K)	8.4	1.178		
Lithium (Li)				
Ammonium (NH_4)				
Alkalies	27.6		21.6	
Calcium (Ca)	12.8	1.791	15.7	2.221
Magnesium (Mg)	9.6	1.342	12.7	1.801
Barium (Ba)				
Strontium (Sr)				
Earths	22.4		28.4	
Iron (Fe)				
Aluminum (Al)				
Manganese (Mn)				
Hydrogen (H)				
Nickel (Ni)				
Cobalt (Co)				
Copper (Cu)		Trace.		Trace.
Cadmium (Cd)				
Lead (Pb)		Trace.		Trace.
Zinc (Zn)		Trace.		Trace.
Metals				
Sum of bases	50.0	6.986	50.0	7.075
Sulphate (SO_4)	2.7	.3773	2.3	.3208
Chloride (Cl)	30.1	4.205	19.3	2.732
Bromide (Br)				
Iodide (I)				
Fluoride (F)				
Nitrate (NO_3)				
Thiosulphate (S_2O_3)				
Strong acids	32.8		21.6	
Carbonate (CO_3)	17.2	2.404	28.4	4.022
Sulphide (S)				
Hydroxyl (OH)				
Arsenate (AsO_4)				
Phosphate (PO_4)				
Weak acids	17.2		28.4	
Sum of acids	50.0	6.986	50.0	7.075
Total value of reacting solids	100.0	13.972	100.0	14.15
BASE ANALYSIS. (Summary by weight, in parts per million.)				
Total weight of reacting solids	474		494	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	9		18	
Total dissolved solids	483		512	
Gases:				
Hydrogen sulphide (H_2S)	Present.		Present.	
Carbon dioxide (CO_2)	6			

TABLE 6.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kansas.*

No. in synoptical table	5		13		33		78	
Source of water	Columbus well		Cherokee well		Fort Scott well		Pittsburg reservoir.	
Temperature	24° C.=75.2° F.		22° C.=71.5° F.		19.7° C.=67.5° F.			
PROPERTIES.								
Primary salinity	16.0		51.0		79.0		37.4	
Secondary salinity			.6		.8		10.0	
Tertiary salinity								
Primary alkalinity	40.2							
Secondary alkalinity	43.8		48.4		12.2		52.6	
Tertiary alkalinity								
	100.0		100.0		100.0		100.0	
Chloride salinity	11.0		34.6		87.2		27.0	
Sulphate salinity	3.4		17.0		.6		20.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	27.5	5.003	24.6	5.699	39.5	23.92	17.3	3.219
Potassium (K)	.5	.08704	.9	.2176		Trace.	1.4	.2675
Lithium (Li)	.1	.01441				Trace.		
Ammonium (NH_4)								
Alkalies	28.1		25.5		39.5		18.7	
Calcium (Ca)	11.9	2.161	13.4	3.104	5.7	3.468	18.4	3.411
Magnesium (Mg)	10.0	1.817	11.1	2.573	4.8	2.910	12.9	2.404
Barium (Ba)								
Strontium (Sr)		Trace.						
Earths	21.9		24.5		10.5		31.3	
Iron (Fe)								
Aluminum (Al)								
Manganese (Mn)								
Hydrogen (H)								
Nickel (Ni)								
Cobalt (Co)								
Copper (Cu)		Trace.						Trace.
Cadmium (Cd)								
Lead (Pb)		Trace.						Trace.
Zinc (Zn)		Trace.						Trace.
Metals								
Sum of bases	50.0	9.082	50.0	11.59	50.0	30.30	50.0	9.301
Sulphate (SO_4)	1.7	.2998	12.8	2.963	.3	.2082	10.2	1.899
Chloride (Cl)	5.5	1.001	11.5	2.659	43.6	26.41	13.5	2.503
Bromide (Br)								
Iodide (I)								
Fluoride (F)								
Nitrate (NO_3)								
Thiosulphate (S_2O_3)	.8	.1498						
Strong acids	8.0		24.3		43.9		23.7	
Carbonate (CO_3)	42.0	7.631	25.7	5.972	5.5	3.304	26.3	4.899
Sulphide (S)								
Hydroxyl (OH)					.6	.3743		
Arsenate (AsO_4)								
Phosphate (PO_4)								
Weak acids	42.0		25.7		6.1		26.3	
Sum of acids	50.0	9.082	50.0	11.59	50.0	30.30	50.0	9.301
Total value of reacting solids	100.0	18.164	100.0	23.18	100.0	60.60	100.0	18.602
BASE ANALYSIS. (Summary by weight, in parts per million.)								
Total weight of reacting solids	708		834		1,832		661	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	8		13		24		12	
Total dissolved solids	716		847		1,856		673	
Gases:								
Hydrogen sulphide (H_2S)	11		Abundant.		Trace.		Present.	
Carbon dioxide (CO_2)					Trace.		26	

TABLE 6.—*Chemical character and geochemical properties of zinc-bearing and related waters in Kansas*—Continued.

No. in synoptical table	90		102		108		109	
Source of water	Pittsburg well		Chico Spring		Pittsburg well No. 3.		Cave Spring.	
Temperature			14.8° C.=58.6° F.				15° C.=59° F.	
PROPERTIES.								
Primary salinity	37.8		5.0		31.4		8.8	
Secondary salinity	4.4		43.6		22.8		56.0	
Tertiary salinity								
Primary alkalinity								
Secondary alkalinity	57.8		51.4		45.8		35.2	
Tertiary alkalinity								
	100.0		100.0		100.0		100.0	
Chloride salinity	20.4		3.4		28.8		6.4	
Sulphate salinity	21.8		45.2		25.4		58.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	18.9	2.871	2.5	0.1479	15.3	2.595	4.4	0.1088
Potassium (K)					.4	.06426		
Lithium (Li)								
Ammonium (NH_4)								
Alkalies	18.9		2.5		15.7		4.4	
Calcium (Ca)	15.5	2.495	38.2	2.285	19.2	3.272	40.2	.9880
Magnesium (Mg)	14.6	2.219	9.3	.5590	15.1	2.568	5.4	.1315
Barium (Ba)								
Strontium (Sr)								
Earths	31.1		47.5		34.3		45.6	
Iron (Fe)								
Aluminum (Al)								
Manganese (Mn)								
Hydrogen (H)								
Nickel (Ni)								
Cobalt (Co)								
Copper (Cu)		Trace.				Trace.		
Cadmium (Cd)								
Lead (Pb)		Trace.				Trace.		
Zinc (Zn)		Trace.		Trace.		Trace.		
Metals								
Sum of bases	50.0	7.585	50.0	2.992	50.0	8.499	50.0	1.228
Sulphate (SO_4)	10.9	1.643	22.6	1.353	12.7	2.158	29.2	.7162
Chloride (Cl)	10.2	1.551	1.7	.09870	14.4	2.451	3.2	.07896
Bromide (Br)								
Iodide (I)								
Fluoride (F)								
Nitrate (NO_3)								
Thiosulphate (S_2O_3)								
Strong acids	21.1		24.3		27.1		32.4	
Carbonate (CO_3)	28.9	4.391	25.7	1.540	22.9	3.891	17.6	.4331
Sulphide (S)								
Hydroxyl (OH)								
Arsenate (AsO_4)								
Phosphate (PO_4)								
Weak acids	28.9		24.3		22.9		17.6	
Sum of acids	50.0	7.585	50.0	2.992	50.0	8.499	50.0	1.228
Total value of reacting solids	100.0	15.170	100.0	5.984	100.0	16.998	100.0	2.456
BASE ANALYSIS. (Summary by weight, in parts per million.)								
Total weight of reacting solids	545		219		587		88	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	3		24		15		22	
Total dissolved solids	548		243		602		110	
Gases:								
Hydrogen sulphide (H_2S)	Present.				3			
Carbon dioxide (CO_2)					18.8			

TABLE 7.—*Chemical character and geochemical properties of zinc-bearing and related waters in Oklahoma.*

No. in synoptical table	15		18		20	
Source of water	Vinita well		Church mine		Nowata well.	
PROPERTIES.						
Primary salinity	65.0		53.0		53.6	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	24.8		13.6		8.0	
Secondary alkalinity	10.2		33.4		38.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	63.0		53.0		52.6	
Sulphate salinity	2.0				1.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	44.9	15.33	33.3	4.167	30.8	588.5
Potassium (K)						
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	44.9		33.3		30.8	
Calcium (Ca)	3.1	1.060	12.0	1.507	14.6	279.6
Magnesium (Mg)	2.0	.6984	4.7	.5918	4.6	87.64
Barium (Ba)						
Strontium (Sr)						
Earths	5.1		16.7		19.2	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)	Trace.					
Cadmium (Cd)						
Lead (Pb)	Trace.					
Zinc (Zn)	Trace.			Trace.		
Metals						
Sums of bases	50.0	17.09	50.0	6.266	50.0	955.7
Sulphate (SO_4)	1.0	.3591		Present.	.5	8.822
Chloride (Cl)	31.5	10.76	26.5	3.322	26.3	502.4
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)				Present.		
Thiosulphate (S_2O_3)						
Strong acids	32.5		26.5		26.8	
Carbonate (CO_3)	17.5	5.969	23.5	2.944	23.2	444.5
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	17.5		23.5		23.2	
Sum of acids	50.0	17.09	50.0	6.266	50.0	955.7
Total value of reacting solids	100.0	34.18	100.0	12.53	100.0	1,911.4
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	1,145		431		65,235	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	11		12		106	
Total dissolved solids	1,156		443		65,341	
Gases:						
Hydrogen sulphide (H_2S)	1		8		24	
Carbon dioxide (CO_2)			Trace.			

TABLE 7.—*Chemical character and geochemical properties of zinc-bearing and related waters in Oklahoma*—Continued.

No. in synoptical table	23		25		30	
Source of water	Afton well		Whitaker Park well.		Chapman & Lennan mine.	
PROPERTIES.						
Primary salinity	68.0		88.4		58.4	
Secondary salinity					7.0	
Tertiary salinity						
Primary alkalinity	4.6		.2			
Secondary alkalinity	27.4		11.4		34.6	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	65.6		87.8		58.6	
Sulphate salinity	2.4		.6		6.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	36.3	6.898	43.9	110.7	29.2	3.841
Potassium (K)			.4	.8704		Trace.
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	36.3		44.3		29.2	
Calcium (Ca)	8.2	1.556	3.6	9.157	13.6	1.797
Magnesium (Mg)	5.5	1.058	2.1	5.347	7.2	.9420
Barium (Ba)						
Strontium (Sr)						
Earths	13.7		5.7		20.8	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				.0		.0
Cadmium (Cd)						
Lead (Pb)				Trace.		.0
Zinc (Zn)				Trace.		.0
Metals						
Sum of bases	50.0	9.512	50.0	126.1	50.0	6.580
Sulphate (SO_4)	1.2	.2362	.3	.8424	3.4	.4447
Chloride (Cl)	32.8	6.233	43.9	110.7	29.3	3.863
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	34.0		44.2		32.7	
Carbonate (CO_3)	16.0	3.043	5.8	14.59	17.3	2.272
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	16.0		5.8		17.3	
Sum of acids	50.0	9.512	50.0	126.1	50.0	6.580
Total value of reacting solids	100.0	19.02	100.0	252.2	100.0	13.16
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	620		7,683		433	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	14		13		10	
Total dissolved solids	634		7,696		443	
Gases:						
Hydrogen sulphide (H_2S)	10		50		2	
Carbon dioxide (CO_2)	4		93		22	

TABLE 7.—*Chemical character and geochemical properties of zinc-bearing waters in Oklahoma*—Continued.

No. in synoptical table	34		45		46	
Source of water	Miami ice plant		Brown well		Radium well.	
PROPERTIES.						
Primary salinity	50.2		82.2		82.6	
Secondary salinity	9.6		16.6		17.0	
Tertiary salinity						
Primary alkalinity						
Secondary alkalinity	40.2		1.2		.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	56.6		98.8		99.6	
Sulphate salinity	3.2					
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	25.1	2.854	41.1	524.2	41.3	537.8
Potassium (K)						Trace.
Lithium (Li)						Trace.
Ammonium (NH_4)						
Alkalies	25.1		41.1		41.3	
Calcium (Ca)	14.1	1.605	5.8	74.14	5.6	73.81
Magnesium (Mg)	10.8	1.225	3.1	39.24	3.1	40.11
Barium (Ba)						
Strontium (Sr)						
Earths	24.9		8.9		8.7	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				Trace.		Trace.
Cadmium (Cd)						
Lead (Pb)				Trace.		Trace.
Zinc (Zn)				Trace.		Trace.
Metals						
Sum of bases	50.0	5.684	50.0	637.6	50.0	651.7
Sulphate (SO_4)	1.6	.1874				
Chloride (Cl)	28.3	3.215	49.4	629.8	49.8	649.3
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	29.9		49.4		49.8	
Carbonate (CO_3)	20.1	2.282	.6	7.787	.2	2.410
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	20.1		.6		.2	
Sum of acids	50.0	5.684	50.0	637.6	50.0	651.7
Total value of reacting solids	100.0	11.37	100.0	1,275.0	100.0	1,303.0
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	375		36,823		37,502	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	9				14	
Total dissolved solids	384		36,823		37,516	
Gases:						
Hydrogen sulphide (H_2S)	Present.		Abundant.		118	
Carbon dioxide (CO_2)	3					

TABLE 7.—*Chemical character and geochemical properties of zinc-bearing waters in Oklahoma*—Continued.

No. in synoptical table	69		71		77	
Source of water	Bernice well.		Chapman & Lennan mine.		Fairland well.	
PROPERTIES.						
Primary salinity	10.6		44.4		33.2	
Secondary salinity					6.6	
Tertiary salinity						
Primary alkalinity	5.8					
Secondary alkalinity	83.6		55.6		60.2	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	5.8		44.4		39.8	
Sulphate salinity	4.8					
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	6.1	0.4559	22.2	4.052	16.6	1.673
Potassium (K)	2.1	.1560				
Lithium (Li)						
Ammonium (NH_4)						
Alkalies	8.2		22.2		16.6	
Calcium (Ca)	34.1	2.567	20.2	3.683	18.0	1.812
Magnesium (Mg)	7.7	.5803	7.6	1.397	15.4	1.552
Barium (Ba)						
Strontium (Sr)						
Earths	41.8		27.8		33.4	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		.0				
Cadmium (Cd)						
Lead (Pb)		.0				
Zinc (Zn)		.0		.0		
Metals						
Sum of bases	50.0	3.760	50.0	9.132	50.0	5.037
Sulphate (SO_4)	2.4	.1768		Trace.		
Chloride (Cl)	2.9	.2200	22.2	4.052	19.9	2.004
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	5.3		22.2		19.9	
Carbonate (CO_3)	44.7	3.363	27.8	5.080	30.1	3.033
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	44.7		27.8		30.1	
Sum of acids	50.0	3.760	50.0	9.132	50.0	5.037
Total value of reacting solids	100.0	7.520	100.0	18.26	100.0	10.07
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	297		637		350	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	18		11			
Total dissolved solids	315		648		350	
Gases:						
Hydrogen sulphide (H_2S)	Present.		Abundant.			
Carbon dioxide (CO_2)	39		22			

TABLE 8.—*Chemical character and geochemical properties of zinc-bearing and related waters in Colorado.*

No. in synoptical table	3		6		10	
Source of water	Geyser mine (2,000 feet).		Doughty Black Spring.		Poncha Spring.	
Temperature	80° F		17.5° C.=63.5° F		90°–168° F.	
PROPERTIES.						
Primary salinity	14.8		44.6		28.4	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	47.8		38.0		56.4	
Secondary alkalinity	37.4		17.4		15.2	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	9.0		35.4		7.8	
Sulphate salinity	5.8		8.8		20.6	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	26.6	31.30	39.9	51.96	41.8	8.670
Potassium (K)	4.3	5.069	1.1	1.504	.6	.1153
Lithium (Li)	.4	.4107	.2	.2276		
Ammonium (NH_4)			.1	.0719		
Alkalies	31.3		41.3		42.4	
Calcium (Ca)	6.2	7.306	4.8	6.304	7.6	1.572
Magnesium (Mg)	12.4	14.604	3.8	5.000		
Barium (Ba)						
Strontium (Sr)	.1	.04446	.1	.0798		
Earths	18.7		8.7		7.6	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)	.0	.00063				
Cadmium (Cd)						
Lead (Pb)	.0	.01304				
Zinc (Zn)	.0	.0104		Trace.		Trace.
Metals						
Sum of bases	50.0	58.76	50.0	65.15	50.0	10.36
Sulphate (SO_4)	2.9	3.367	4.4	5.686	10.3	2.140
Chloride (Cl)	4.5	5.256	17.7	23.01	3.9	.7981
Bromide (Br)		Trace.	.1	.1838		
Iodide (I)		Trace.		Trace.		
Fluoride (F)		Trace.				
Nitrate (NO_3)	.0	.02576				
Thiosulphate (S_2O_3)			.1	.1926		
Strong acids	7.4		22.3		14.2	
Carbonate (CO_3)	42.6	50.11	27.7	36.08	35.8	7.422
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)		Trace.		Trace.		
Weak acids	42.6		27.7		35.8	
Sum of acids	50.0	58.76	50.0	65.15	50.0	10.36
Total value of reacting solids	100.0	117.5	100.0	130.3	100.0	20.72
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	4,655		4,766		820	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	31		35		57	
Total dissolved solids	4,686		4,801		877	
Gases:						
Hydrogen sulphide (H_2S)			49			
Carbon dioxide (CO_2)			977			

TABLE 8.—*Chemical character and geochemical properties of zinc-bearing and related waters in Colorado*—Continued.

No. in synoptical table	11		12		14	
Source of water	Wagon Wheel Gap Spring.		Cold Sulphur Spring.		Doughty Drinking Spring.	
Temperature	135° F.					
PROPERTIES.						
Primary salinity	21.4		32.6		58.0	
Secondary salinity						
Tertiary salinity						
Primary alkalinity	51.2		34.8		26.6	
Secondary alkalinity	27.4		32.6		15.4	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	7.6		5.4		34.8	
Sulphate salinity	13.8		27.2		23.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	31.1	15.09	30.8	14.94	40.4	45.86
Potassium (K)	2.8	1.331	2.9	1.398	1.4	1.576
Lithium (Li)	2.4	1.153			.4	.4409
Ammonium (NH_4)					.1	.0664
Alkalies	36.3		33.7		42.3	
Calcium (Ca)	4.7	2.295	11.3	5.479	4.6	5.272
Magnesium (Mg)	9.0	4.357	5.0	2.400	2.8	3.230
Barium (Ba)					.2	.1920
Strontium (Sr)				Trace.	.1	.1506
Earths	13.7		16.3		7.7	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				Trace.		
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)		Trace.		Trace.		Trace.
Metals						
Sum of bases	50.0	24.23	50.0	24.22	50.0	56.80
Sulphate (SO_4)	6.9	3.352	13.6	6.615	11.5	13.02
Chloride (Cl)	3.8	1.861	2.7	1.289	17.4	19.76
Bromide (Br)					.1	.0650
Iodide (I)						Trace.
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	10.7		16.3		29.0	
Carbonate (CO_3)	39.3	19.02	33.7	16.32	21.0	23.94
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)						
Weak acids	39.3		33.7		21.0	
Sum of acids	50.0	24.23	50.0	24.22	50.0	56.80
Total value of reacting solids	100.0	48.46	100.0	48.44	100.0	113.6
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	1,893		1,896		4,077	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	10		61		33	
Total dissolved solids	1,903		1,957		4,110	
Gases:						
Hydrogen sulphide (H_2S)					47	
Carbon dioxide (CO_2)			28		2,058	

TABLE 8.—*Chemical character and geochemical properties of zinc-bearing and related waters in Colorado*—Continued.

No. in synoptical table	31		70		79	
Source of water	Yampa Spring		Royal Gorge Cold Spring.		Boulder city water	
Temperature	120° F		70° F			
PROPERTIES.						
Primary salinity	90.0		34.2		20.8	
Secondary salinity	7.4				10.2	
Tertiary salinity						
Primary alkalinity			.4			
Secondary alkalinity	2.6		65.4		69.0	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	89.6		23.8		15.6	
Sulphate salinity	7.8		10.4		15.4	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	44.3	319.8	16.3	6.968	8.2	0.08856
Potassium (K)	.7	4.731	.9	.3669	2.2	.0231
Lithium (Li)	.0	.0556	.1	.0282		Trace.
Ammonium (NH_4)						
Alkalies	45.0		17.3		10.4	
Calcium (Ca)	3.9	28.37	21.3	9.108	30.9	.3329
Magnesium (Mg)	1.1	7.809	11.1	4.760	8.6	.09298
Barium (Ba)						
Strontium (Sr)			.3	.1196	.1	.00128
Earths	5.0		32.7		39.6	
Iron (Fe)						
Aluminum (Al)						
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)				Trace.		
Cadmium (Cd)						
Lead (Pb)						
Zinc (Zn)			.0	.0084		Trace.
Metals						
Sum of bases	50.0	360.8	50.0	21.36	50.0	.5388
Sulphate (SO_4)	3.9	27.96	5.2	2.226	7.7	.08286
Chloride (Cl)	44.8	323.6	11.9	5.078	7.8	.08357
Bromide (Br)	.0	.0937				
Iodide (I)		Trace.				
Fluoride (F)		Trace.				
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	48.7		17.1		15.5	
Carbonate (CO_3)	1.3	9.112	32.9	14.06	34.5	.3724
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)		Trace.		Trace.		
Weak acids	1.3		32.9		34.5	
Sum of acids	50.0	360.8	50.0	21.36	50.0	.5388
Total value of reacting solids	100.0	721.6	100.0	42.72	100.0	1.0776
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	21,587		1,566		40	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_2, etc.)	34		30		9	
Total dissolved solids	21,621		1,596		49	
Gases:						
Hydrogen sulphide (H_2S)	Present.					
Carbon dioxide (CO_2)	Present.		920			

Table 8.—*Chemical character and geochemical properties of zinc-bearing and related waters in Colorado*—Continued.

No. in synoptical table	80		114	
Source of water	Geyser mine (500 feet).		Black Hawk well.	
PROPERTIES.				
Primary salinity	23.8		7.2	
Secondary salinity			73.4	
Tertiary salinity			16.4	
Primary alkalinity	15.4			
Secondary alkalinity	60.8			
Tertiary alkalinity			3.0	
	100.0		100.0	
Chloride salinity	4.8		3.8	
Sulphate salinity	19.0		93.2	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	16.7	1.583	3.5	1.210
Potassium (K)	2.9	.2714	.1	.04291
Lithium (Li)				
Ammonium (NH_4)				
Alkalies	19.6		3.6	
Calcium (Ca)	19.7	1.866	24.8	8.593
Magnesium (Mg)	10.6	1.007	11.9	4.141
Barium (Ba)				
Strontium (Sr)				
Earths	[a] 30.4		36.7	
Iron (Fe)			4.2	1.453
Aluminum (Al)				
Manganese (Mn)			3.9	1.351
Hydrogen (H)				
Nickel (Ni)				
Cobalt (Co)				
Copper (Cu)		Trace.		Trace.
Cadmium (Cd)				
Lead (Pb)		Trace.		
Zinc (Zn)	[a] .1	.00612	1.6	.5463
Metals			9.7	
Sum of bases	50.0	4.734	50.0	17.34
Sulphate (SO_4)	9.5	.8994	46.6	16.16
Chloride (Cl)	2.4	.2228	1.9	.6695
Bromide (Br)				
Iodide (I)				
Fluoride (F)				
Nitrate (NO_3)				
Thiosulphate (S_2O_3)				
Strong acids	11.9		48.5	
Carbonate (CO_3)	38.1	3.612	1.5	.5105
Sulphide (S)				
Hydroxyl (OH)				
Arsenate (AsO_4)				
Phosphate (PO_4)				
Weak acids	38.1		1.5	
Sum of acids	50.0	4.734	50.0	17.34
Total value of reacting solids	100.0	9.468	100.0	34.68
BASE ANALYSIS. (Summary by weight, in parts per million.)				
Total weight of reacting solids	368		1,153	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	29		37	
Total dissolved solids	397		1,190	
Gases:				
Hydrogen sulphide (H_2S)				
Carbon dioxide (CO_2)				

[a] The reacting value of the zinc is included with that of the earths.

TABLE 9.—*Chemical character and geochemical properties of zinc-bearing and related waters in Michigan, Montana, Nevada, and California.*

No. in synoptical table	17		60		81	
Source of water	Steamboat Springs.		Mizpah mine		Federal Loan mine.	
Temperature	75°-84.5° C					
PROPERTIES.						
Primary salinity	87.6		61.8		9.0	
Secondary salinity			11.8			
Tertiary salinity	11.2				13.2	
Primary alkalinity	1.2		25.4		77.8	
Secondary alkalinity			1.0			
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	79.8		9.4		3.2	
Sulphate salinity	7.8		64.2		5.8	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	44.0	29.66	30.5	6.473	10.6	0.5829
Potassium (K)	3.9	2.645	.4	.08704	.5	.0256
Lithium (Li)	1.5	1.031				
Ammonium (NH_4)						
Alkalies	49.4		30.9		11.1	
Calcium (Ca)	.5	.3416	16.2	3.433	30.4	1.677
Magnesium (Mg)	.1	.0233	2.4	.5179	8.5	.4685
Barium (Ba)						
Strontium (Sr)						
Earths	.6		18.6		38.9	
Iron (Fe)			.1	.02506		
Aluminum (Al)			.4	.07749		
Manganese (Mn)						
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)						
Cadmium (Cd)						
Lead (Pb)						Trace.
Zinc (Zn)				Trace.		
Metals			.5			
Sum of bases	50.0	33.70	50.0	10.61	50.0	2.754
Sulphate (SO_4)	3.9	2.650	32.1	6.812	2.9	.1603
Chloride (Cl)	39.9	26.86	4.7	1.004	1.6	.08911
Bromide (Br)						
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)				Trace.		
Thiosulphate (S_2O_3)						Present.
Strong acids	43.8		36.8		4.5	
Carbonate (CO_3)	5.7	.3850	13.2	2.797	44.2	2.436
Sulphide (S)	.3	.2039			1.3	.06864
Hydroxyl (OH)						
Arsenate (AsO_4)	.2	.1082				
Phosphate (PO_4)	.0	.02660				
Weak acids	6.2		13.2		45.5	
Sum of acids	50.0	33.70	50.0	10.61	50.0	2.754
Total value of reacting solids	100.0	67.40	100.0	21.22	100.0	5.508
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	2,121		762		214	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	579		65		37	
Total dissolved solids	2,700		827		251	
Gases:						
Hydrogen sulphide (H_2S)	1				Present.	
Carbon dioxide (CO_2)						

TABLE 9.—*Chemical character and geochemical properties of zinc-bearing and related waters in Michigan, Montana, Nevada, and California*—Continued.

No. in synoptical table	104		115		111	
Source of water	Gagnon mine		Tamarack, jr., mine.		Green Mountain mine.	
PROPERTIES.						
Primary salinity	10.2		18.4		8.2	
Secondary salinity	85.0		80.0		71.6	
Tertiary salinity						
Primary alkalinity	4.6		1.6		19.4	
Secondary alkalinity	.2				.8	
Tertiary alkalinity						
	100.0		100.0		100.0	
Chloride salinity	62.6		96.2		1.8	
Sulphate salinity	32.6		.0		78.0	
REACTING VALUES.	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*	*Per cent.*	*Parts per million.*
Sodium (Na)	4.7	3.602	9.1	33.66	3.3	0.7047
Potassium (K)	.4	.2918	.1	.5560	.8	.1818
Lithium (Li)			.0	.08968		
Ammonium (NH_4)						
Alkalies	5.1		9.2		4.1	
Calcium (Ca)	33.7	25.55	40.2	148.7	34.8	7.545
Magnesium (Mg)	11.1	8.434	.3	1.087	10.7	2.318
Barium (Ba)						
Strontium (Sr)			.1	.3974		
Earths	44.8		[a]40.6		45.5	
Iron (Fe)	.0	.01432			.3	.06444
Aluminum (Al)						
Manganese (Mn)	.1	.05100			.1	.01821
Hydrogen (H)						
Nickel (Ni)						
Cobalt (Co)						
Copper (Cu)		Trace.	.1	.3775		Trace.
Cadmium (Cd)		.0				
Lead (Pb)		.0				
Zinc (Zn)		.0	[a].1	.2447	.0	.0092
Metals	.1				.4	
Sum of bases	50.0	37.94	50.0	185.1	50.0	10.84
Sulphate (SO_4)	16.3	12.35	.0	.0175	39.0	8.463
Chloride (Cl)	31.3	23.77	48.1	178.3	.9	.1918
Bromide (Br)			1.1	3.975		
Iodide (I)						
Fluoride (F)						
Nitrate (NO_3)						
Thiosulphate (S_2O_3)						
Strong acids	47.6		49.2		39.9	
Carbonate (CO_3)	2.4	1.823	.8	2.819	10.1	2.188
Sulphide (S)						
Hydroxyl (OH)						
Arsenate (AsO_4)						
Phosphate (PO_4)		Trace.				Trace.
Weak acids	2.4		.8		10.1	
Sum of acids	50.0	37.94	50.0	185.1	50.0	10.84
Total value of reacting solids	100.0	75.88	100.0	370.2	100.0	21.68
BASE ANALYSIS. (Summary by weight, in parts per million.)						
Total weight of reacting solids	2,258		10,173		752	
Colloids (SiO_2, Al_2O_3, Fe_2O_3, BO_3, etc.)	30		12		23	
Total dissolved solids	2,288		10,185		775	
Gases:						
Hydrogen sulphide (H_2S)						
Carbon dioxide (CO_2)					2.72	

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[a] The reacting value of the zinc is included with that of the earths.

CLASSIFICATION OF ZINC-BEARING AND RELATED WATERS.

When the number of quantitative analyses of waters available for study and comparison reaches that here presented it becomes necessary to group them according to some well-considered scheme of classification. The scheme here adopted is based on the principles of water characterization just set forth and includes only those subgroups that are represented in the analyses here given. It has been devised solely to meet the requirements of the present investigation and is not presented for general use, although, by logical expansion and further subdivision, it might be made applicable to nearly all natural waters. In this scheme the principal classes are founded on the preponderating groups of bases. These classes are divided according to the nature of the preponderating acid radicles held in equilibrium with these bases, and are subdivided according to the nature of the salinity. They are further subdivided according to the kind of accessory alkalinity or salinity. A similar scheme might classify the first division by alkalinity or salinity and the subdivisions by the groups of bases. Such a classification would somewhat resemble that adopted by Peale,[1] though in his plan the waters were classified according to the weights of the different constituents rather than according to their molecular ratios, as in the two schemes proposed above. Both these schemes were tried by the writer, but the one here adopted seemed to work out best in actual practice with the waters under consideration.

In the following key to the scheme of classification adopted and in this report generally, the terms primary, secondary, and tertiary, when applied to waters, are used in the ordinal sense in which their use has been established by Palmer,[2] Spencer,[3] Emmons and Harrington,[4] Van Winkle,[5] Waring,[6] and Clapp,[7] in connection with the radicles of bases in solution in waters. Thus we have primary, secondary, and tertiary salinity, alkalinity, bases, and waters, all members of related series, each determined by the predominant groups of positive or base radicles. The reader must not confuse these terms with the terms primary and secondary as they are applied to original and derived ore deposits, for as applied to ores they have a genetic significance, whereas their use here is purely ordinal.

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[5] Van Winkle, Walton, Quality of the surface waters of Washington: U. S. Geol. Survey Water-Supply Papcr 339, pp. 34–35, 1914; Quality of the surface waters of Oregon: U. S. Geol. Survey Water-Supply Paper 363, pp. 37–38, 1914.

[6] Waring, G. A., Springs of California: U. S. Geol. Survey Water-Supply Paper 338, pp. 22–23, 1914.

[7] Clapp, C. H., Sharp Point hot spring, Vancouver Island, British Columbia: Canada Dept. Mines Summary Rept. Geol. Survey for 1913, pp. 80–83, 1914.

Key to classification of zinc-bearing and related waters.

Predominant bases.	Predominant character.	Subordinate character.	Accessory character.	Section.
Primary waters (primary bases predominant).	Alkaline	Chloride salinity		A
		Sulphate salinity		B
	Saline	Chloride salinity	Primary alkalinity	C
			Secondary alkalinity	D
		Sulphate salinity	Primary alkalinity	E
			Secondary alkalinity	F
Secondary waters (secondary bases predominant).	Alkaline	Chloride salinity	Primary salinity	G
			Secondary salinity	
		Sulphate salinity	Primary salinity	H
			Secondary salinity	I
	Saline	Chloride salinity	Primary salinity	J
			Secondary salinity	K
		Sulphate salinity	Primary salinity	L
			Secondary salinity	M
			Tertiary salinity	N
Tertiary waters (tertiary bases predominant).	Saline	Sulphate salinity	Tertiary alkalinity	O
			Tertiary salinity	P

SYNOPTICAL OUTLINE OF ZINC-BEARING WATERS.

The geochemical scheme for interpreting water analyses lends itself admirably to the presentation in tabular form of the essential properties of a series of waters. The synoptical table below shows the character of 119 waters, most of them from the Joplin region and adjoining territory, but many from distant States or from foreign countries. Nearly all these waters carry zinc or lead. A zero (0) in the last column opposite the designation of any water indicates that tests for these metals gave negative results. A question mark (?) in the last column opposite the designation of a water that has not been tested for these metals but is closely related in character, in geographic location, and in geologic environment to waters known to be zinc-bearing indicates that it may probably carry these metals.

A somewhat similar scheme was used by Pošepný,[1] but he combined the chlorides of the alkalies and earths and gave them separately from the sulphates. Another essential difference in presentation is that the properties were expressed by Pošepný in their mass weights instead of in reaction values, as in the table here presented. The undesirability of the use of mass weights is dwelt upon in the quotation from Palmer. In an analysis expressed in that way one must either make a mental estimate of the reacting values of the salts or must form a false conception of the proportions of the salts in the solution.

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[1] Pošepný, Franz, The genesis of ore deposits: Am. Inst. Min. Eng. Trans., vol. 23, p. 234, 1894.

Synoptical table of zinc-bearing waters.

Primary waters.—Primary bases (alkalies) predominant.

No.	Source.	Salinity.			Alkalinity.			Chloride salinity.	Sulphate salinity.	Zinc content.
		Primary.	Secondary.	Tertiary.	Primary.	Secondary.	Tertiary.			
	SECTION A.—*Predominantly alkaline with chloride salinity in excess.*									
1	Lindenquelle, Germany	14.0			56.2	29.8		10.4	3.6	
2	"Du Rocher" Spring, France	33.0			55.2	11.8		27.2	5.8	
3	Geyser mine, Colo., 2,000-foot level	14.8			47.8	37.4		9.0	5.8	
4	Grosser Sprudel, Germany	11.2			46.2	42.6		6.6	4.6	
5	Columbus well, Kans	16.0			40.2	43.8		11.0	3.4	
6	Doughty Black Spring, Colo	44.6			38.0	17.4		35.4	8.8	
7	Arienheller Sprudel, Germany	34.2			35.2	30.6		29.4	4.6	
8	Thompson Spring, N. C	30.0			25.8	44.2		18.6	10.8	
	SECTION B.—*Predominantly alkaline with sulphate salinity in excess.*									
9	Kainzen-(St. Antons) Quelle, Germany	8.4			87.4	4.2		2.0	6.2	
10	Poncha Spring No. 1, Colo	28.4			56.4	15.2		7.8	20.6	
11	Wagon Wheel Gap hot spring No. 1, Colo	21.4			51.2	27.4		7.6	13.8	
12	Cold Sulphur Spring, Idaho Springs, Colo	32.6			34.8	32.6		5.4	27.2	
13	Cherokee well, Kans	48.6			2.4	49.0		23.0	25.6	(?)
	SECTION C.—*Predominantly saline with chloride salinity in excess and accessory primary alkalinity.*									
14	Doughty Drinking Spring, Colo	58.0			26.6	15.4		34.8	23.0	
15	Frisco well, Vinita, Okla	65.0			24.8	10.2		63.0	2.0	
16	Rhenser Sprudel, Germany	57.6			21.6	20.8		37.8	19.8	
17	Steamboat Springs, Nev	87.6			11.2	1.2		79.8	7.8	(?)
	SECTION D.—*Predominantly saline with chloride salinity in excess and accessory secondary alkalinity or accessory secondary salinity.*									
18	Church mine, Okla	53.0			13.6	33.4		53.0		
19	Renfro well, Ky	55.6			10.2	34.2		57.4	8.2	
20	Nowata well, Okla	53.6			8.0	38.4		52.6	1.0	(?)
21	Sanders well, Ky	65.6			7.4	27.0		36.0	29.6	
22	Sadieville public well, Ky	66.6			5.0	28.4		65.6	1.0	
23	Afton well, Okla	68.0			4.6	27.4		65.6	2.4	
24	Hopkinsville well, Ky	79.2			.4	20.4		60.6	18.6	
25	Whitaker Park well, Okla	88.4			.2	11.4		87.8	.6	
26	Niederbronn, Germany	74.0	3.8			22.2		76.0	1.8	

Synoptical table of zinc-bearing waters—Continued.

Primary waters.—Primary bases (alkalies) predominant—Continued.

No.	Source.	Salinity.			Alkalinity.			Chloride salinity.	Sulphate salinity.	Zinc content.
		Primary	Secondary.	Tertiary.	Primary.	Secondary.	Tertiary.			
	Section D.—*Predominantly saline with chloride salinity in excess and accessory secondary alkalinity or accessory secondary salinity*—Continued.									
27	Nevada well, Mo.	66.6	5.6			27.8		66.8	5.4	(?)
28	Caddo oil well, La.	91.4	6.2			2.4		77.8	19.8	0
29	Solquelle "Bonifazius," Germany	92.2	6.8			1.0		95.8	3.2	
30	Chapman & Lennan mine water, Okla.	58.4	7.0			34.6		58.6	6.8	0
31	Yampa Spring, Colo.	90.0	7.4			2.6		89.6	7.8	0
32	Clinton well No. 2, Mo.	58.6	8.4			33.0		55.8	11.2	
33	Fort Scott well, Kans.	79.0	8.8			12.2		87.2	.6	(?)
34	Miami well, Okla.	50.2	9.6			40.2		56.6	3.2	(?)
35	White Sulphur Spring, Ark.	55.2	10.4			34.4		60.2	5.4	
36	Estill well, Ky.	86.0	10.6			3.4		96.4	.2	
37	Schönbornsprudel, Germany	75.6	10.8			13.6		73.6	12.8	
38	Silver well, Mo. (upper flow)	75.0	12.0			13.0		75.0	12.0	0
39	Salztrinkquelle, Germany	75.0	12.0			13.0		69.6	17.4	
40	Clinton well No. 3 (Britt), Mo.	62.4	12.4			25.2		66.8	8.0	
41	Elisabethbrunnen, Germany	74.6	12.8			12.6		87.0	.4	
42	Clinton well No. 1, Mo.	65.0	13.8			21.2		70.8	8.0	
43	Martinusquelle, Germany	72.2	14.6			13.2		74.6	12.2	
44	Elisabethquelle, Germany	80.4	16.0			3.6		96.2		
45	Brown well, Okla.	82.2	16.6			1.2		98.8		
46	Radium well, Okla.	82.6	17.0			.4		99.6		
47	Sydney waterworks, New South Wales.	66.4	17.4			16.2		71.2	11.2	
48	Sharp well, Ky.	80.2	17.6			2.2		95.4	2.4	
49	Felix well, Ky.	70.2	18.4			11.4		87.0	1.6	
50	Viktoriaquelle, Germany	80.2	18.4			1.4		98.4		
51	Brunswick well, Mo.	76.2	20.4			3.4		86.4	10.2	(?)
52	Ocean (Dittmar's analysis)	78.6	20.8			.6		90.0	9.2	
53	School well, Warren County, Ky.	71.6	22.0			6.4		76.2	17.4	
54	Grossherzogin-Karolinerquelle, Germany	75.4	22.0			2.6		75.2	22.2	
55	Silver well, Mo. (lower flow)	76.0	23.4			.6		91.4	8.0	0
56	Belcher well, St. Louis, Mo.	73.4	23.6			3.0		89.0	8.0	0
	Section E.—*Predominantly saline with sulphate salinity in excess and accessory primary alkalinity.*									
57	Antonienquelle, Germany	61.6			21.8	16.6		18.2	43.4	
58	Carlsbad Sprudel, Austria-Hungary	60.0			28.2	11.8		20.4	39.6	
59	Néris-les-Bains, France	51.8			35.6	12.6		18.2	33.6	

	SECTION F.—*Predominantly saline with sulphate salinity in excess and accessory secondary alkalinity.*									
60	Mizpah mine, Nev.	61.8	11.8	....	....	25.4	1.0	9.4	64.2	....
61	Lullusquelle bei Hersfeld, Germany	69.2	13.4	....	....	17.4	....	16.4	66.0	....
62	Carolaquelle, Germany	37.8	24.6	....	....	37.6	....	15.6	46.6	....

Secondary waters.—Secondary bases (alkaline earths) predominant.

	SECTION G.—*Predominantly alkaline with chloride salinity in excess and accessory primary salinity.*									
63	Fontinalissprudel, Germany	6.0	....	....	30.6	63.4	....	4.4	1.6	....
64	Cornfield well, Mo.	3.8	....	....	20.6	75.6	....	3.2	.6	(?)
65	Wilson well, Ky.	24.8	....	....	20.2	55.0	....	15.0	9.8	....
66	Minnequa Spring, Pa.	2.8	....	....	13.8	83.4	....	2.6	.2	....
67	Mida Spring, N. C.	10.2	....	....	13.8	76.0	....	3.4	3.2	....
68	Missouri Lead & Zinc Co.'s well (at 1,387 feet)	15.0	....	....	8.6	76.4	....	8.0	7.0	(?)
69	Bernice well, Okla.	10.6	....	....	5.8	83.6	....	5.8	4.8	0
70	Royal Gorge Cold Spring, Colo.	34.2	....	....	.4	65.4	....	23.8	10.4	....
71	Chapman & Lennan mine water, Okla.	44.4	....	....	....	55.6	....	44.4	....	0
72	Sulphur Spring, Ark.	43.2	....	....	....	56.8	....	38.6	4.6	....
73	Coppahaunk Spring, Va.	6.6	0.2	....	....	93.2	....	6.2	.6	....
74	Spring near Louisville, Ky.	3.6	1.0	....	....	95.4	....	2.4	1.2	....
75	Sayre well, Lexington, Ky.	3.8	1.8	....	....	94.4	....	3.8	1.8	....
76	Oronogo well, Mo.	10.2	2.2	....	....	87.6	....	10.2	2.2	(?)
77	Fairland well, Okla.	33.2	6.6	....	....	60.2	....	39.8	....	(?)
78	Pittsburg underground reservoir, Kans.	37.4	10.0	....	....	52.6	....	27.0	20.4	....
79	Boulder city water, Colo.	20.8	10.2	....	....	69.0	....	15.6	15.4	....
	SECTION H.—*Predominantly alkaline with sulphate salinity in excess and accessory primary salinity.*									
80	Geyser mine (500-foot level), Colo.	23.8	....	....	15.4	60.8	....	4.8	19.0	....
81	Federal Loan mine water, Cal.	9.0	....	....	13.2	77.8	....	3.2	5.8	....
82	Missouri Lead & Zinc Co.'s well (at 940 feet)	11.6	....	....	8.2	80.2	....	5.6	6.0	(?)
83	Royal Magnesian Spring, Ky.	3.6	....	....	3.8	92.6	....	1.2	6.2	....
84	Freeman Foundry well, Mo.	18.2	....	....	3.4	78.4	....	3.8	14.4	(?)
85	Höllensprudel, Germany	1.2	....	....	2.2	96.6	....	.4	.6	....
86	Fulton well, Mo.	28.8	....	....	2.0	69.2	....	10.8	18.0	....
87	Cox Spring, Mo.	5.2	.4	....	....	94.4	....	2.0	3.6	0
88	Harrington well, Mo.	10.6	.6	....	....	88.8	....	4.4	6.8	....
89	Providence well, Mo.	7.2	3.8	....	....	89.0	....	1.4	9.6	....
90	Pittsburg waterworks, Kans.	37.8	4.4	....	....	57.8	....	20.4	21.8	....
91	Alba well, Mo.	6.6	5.0	....	....	88.4	....	3.8	7.8	....
92	Redell well, Mo.	15.6	6.2	....	....	78.2	....	7.2	14.6	0
93	Roanoke Red Sulphur Springs, Va.	14.0	13.8	....	....	72.2	....	1.4	26.2	....

Synoptical table of zinc-bearing waters—Continued.

Secondary waters.—Secondary bases (alkaline earths) predominant—Continued.

No.	Source.	Salinity.			Alkalinity.			Chloride salinity.	Sulphate salinity.	Zinc content.
		Primary.	Secondary.	Tertiary.	Primary.	Secondary.	Tertiary.			
	SECTION I.—*Predominantly alkaline with sulphate salinity in excess and accessory secondary salinity.*									
94	Caspar-Heinrich-Quelle, Germany	2.4	3.6	....	....	94.0	....	.8	5.2	....
95	Ash Grove well, Mo.	3.4	9.2	....	....	87.4	....	3.4	9.2	(?)
96	Webb City waterworks, Mo.	4.2	10.4	....	....	85.4	....	7.2	7.4	(?)
97	Eulenhöfer Quelle, Germany	6.8	12.0	....	....	81.2	....	4.4	14.4	....
98	Freeman Foundry well, Mo.	4.8	12.2	....	....	83.0	....	4.4	12.6	(?)
99	Average of 10 southeast Missouri mine waters	15.2	17.6	....	....	67.2	....	13.0	19.8	....
100	Winslow mine water, Mo.	6.6	23.0	....	....	70.4	....	1.2	28.4	0
101	B. & C. mine water, Mo.	5.8	34.2	....	....	60.0	....	1.2	38.8	....
102	Chico Spring, Kans.	5.0	43.6	....	....	51.4	....	3.4	45.2	....
	SECTION J.—*Predominantly saline with chloride salinity in excess and accessory primary salinity.*									
103	Pittsburg well No. 3, Kans.	31.4	22.8	....	....	45.8	....	28.8	25.4	....
	SECTION K.—*Predominantly saline with chloride salinity in excess and accessory secondary salinity.*									
104	Gagnon mine water, Mont.	10.2	85.0	....	....	4.6	0.2	62.6	32.6	....
105	Tamarack, jr., mine water, Mich.	18.4	80.0	....	....	1.6	....	96.2	....	....
106	Johnson well, Tex.	33.6	57.2	....	....	9.2	....	56.0	34.6	....
	SECTION L.—*Predominantly saline with sulphate salinity in excess and accessory primary alkalinity.*									
107	King's mineral spring, Ind.	38.6	58.6	....	....	2.8	....	19.6	77.6	....
	SECTION M.—*Predominantly saline with sulphate salinity in excess and accessory secondary salinity.*									
108	Sphalerite well, Mo.	13.8	44.6	....	....	41.6	....	6.8	51.6	(?)
109	Cave Spring, Kans.	8.8	56.0	....	....	35.2	....	6.4	58.4	(?)
110	Lakeside Spring, Mo.	4.4	64.4	....	....	31.2	....	3.6	65.2	0
111	Green Mountain mine water, Mont.	8.2	71.6	....	....	19.4	.8	1.8	78.0	....
112	Alleghany Spring, Va.	2.8	94.2	....	....	3.0	....	.2	95.2	....

	SECTION N.—*Predominantly saline with sulphate salinity in excess and accessory tertiary salinity.*									
113	Cransac Spring, France	5.0	88.6	6.4				.4	99.6	
114	Black Hawk well, Colo.	7.2	73.4	16.4			3.0	3.8	93.2	
115	Missouri Zinc Fields mine water, Mo	3.6	56.4	31.8			8.2	.4	91.4	

Tertiary waters.—Tertiary bases (metals) predominant.

	SECTION O.—*Predominantly saline with sulphate salinity in excess and accessory tertiary alkalinity.*									
116	Shoal Creek Spring, Mo	3.0	45.2	32.6			19.2	1.0	79.8	
	SECTION P.—*Predominantly saline with sulphate salinity in excess and predominant tertiary salinity.*									
117	Bedford Alum Spring, Va	3.2	28.0	68.8				.4	99.0	
118	Rockbridge Alum Spring No. 2, Va	.6	14.2	85.2				.2	99.8	
119	Guber Spring, Bosnia	2.6	6.2	90.0			1.2	.4	98.6	

The method of using the scheme of classification and the synoptical table here presented can best be illustrated by a simple example. If we take the water from the Chapman & Lennan mine at Miami, Okla., when it was first opened (No. 30 in the table of analyses) we find it characterized as follows:

Primary salinity	58.4
Secondary salinity	7.0
Secondary alkalinity	34.6
	100.0
Chloride salinity	58.6
Sulphate salinity	6.8

The primary bases are evidently predominant and the water is predominantly saline, with chloride salinity and with accessory secondary alkalinity, properties that place it in section D. The analyses in this section are arranged in order of decreasing primary alkalinity and increasing secondary salinity. The water shows 7 per cent of secondary salinity but no primary alkalinity, and this immediately places it between the waters of the Nevada well and the Clinton No. 2 well. This close resemblance of the mine waters at Miami to deep-well waters known to be zinc bearing is discussed on pages 187, 203–205.

The tertiary waters included in sections N, O, and P, at the bottom of the synoptical table, with acid reaction and even with free sulphuric acid, resulting supposedly from the oxidation of metallic sulphides at shallow depths, will of course contain zinc or lead if the original sulphides contained those metals. In this group belong the "alum" springs and the acid mine waters. Section M of the secondary waters, grading over into the group showing tertiary salinity, consists of 3 spring waters, 1 mine water, and 1 deep-well water, the last, through defective casing or otherwise, evidently containing an admixture of surface or mine water. The remaining analyses are pretty well divided between the primary waters and the secondary waters. A general survey of these two divisions shows that zinc is carried by salt sulphur waters and by alkaline carbonate waters, as well as by plain salt waters without hydrogen sulphide and with little alkalinity. In other words, zinc is carried by both sulphureted salt waters and alkaline-earthy carbonate waters, the latter usually containing free carbon dioxide, free hydrogen sulphide, or both. To put it more briefly, most zinc-bearing waters that are not mine waters or "alum springs" waters are either sulphureted, carbonated, or plain salt waters.

Of the 119 waters cited, 73, almost two-thirds of the total, show chloride salinity in excess of sulphate salinity, but, as has been stated, the number of analyses of mine and other sulphate waters was restricted, because they were not considered essential to this discussion.

COMPARISON OF WATERS OF INTERIOR AND BORDER WELLS OF THE OZARK UPLIFT.

The analytical comparison of waters from deep wells in the limestone area of the Ozark uplift with waters from deep wells in the Pennsylvanian shale area surrounding the uplift, though all these wells draw their supply from the Cambrian and Ordovician rocks, reveals some interesting differences, which can best be brought out by a parallel representation of the properties of a short series of waters from each area, and this accordingly has been made in the following table. The arabic numerals in the headings in this table refer to the analyses in the synoptical table. (See pp. 149–153.)

Comparison of the geochemical properties of waters from interior and border wells of the Ozark uplift.

Properties.	Border wells (primary waters).						52	Interior wells (secondary waters).					
	25	27	33	42	45	51		76	88	89	91	92	95
	Pryor Creek.	Nevada.	Fort Scott.	Clinton.	Claremore.	Brunswick.	Ocean water.	Oronogo.	Carthage.	Webb City.	Alba.	Joplin.	Ash Grove.
Primary salinity....	88.4	66.6	79.0	65.0	82.2	76.2	78.6	10.2	10.6	7.2	6.6	15.6	3.4
Secondary salinity..	......	5.6	8.8	13.8	16.6	20.4	20.8	2.2	.6	3.8	5.0	6.2	9.2
Tertiary salinity....	......	......	......	......	......	......	......	......	......	......	......	......	......
Primary alkalinity .	.2	......	......	......	......	......	......	......	......	......	......	......	......
Secondary alkalinity..............	11.4	27.8	12.2	21.2	1.2	3.4	.6	87.6	88.8	89.0	88.4	78.2	87.4
Tertiary alkalinity.	......	......	......	......	......	......	......	......	......	......	......	......	......
Total reacting value (per cent).........	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total reacting value or concentration (parts per million)......	252.0	40.0	61.0	57.0	74.0	269.0	1,211.0	7.0	7.0	7.0	10.0	7.0	7.0
Chloride salinity....	87.8	66.8	87.2	70.8	98.8	86.4	90.0	10.2	4.4	1.4	3.8	7.2	3.4
Sulphate salinity...	.6	5.4	.6	8.0	0	10.2	9.2	2.2	6.8	9.6	7.8	14.6	9.2
Ratio of rCa to rMg[a]	1:.58	1:.67	1:.84	1:.72	1:.53	1:.72	1:.53	1:.62	1:.71	1:.72	1:.13	1:.52	1:.80
	Average ratio of rCa to rMg=1: 0.677.							Average ratio of rCa to rMg=1: 0.583.					

[a] rCa, rMg indicate the reacting weights of calcium and magnesium, respectively.

As will be observed, the border well waters are high in primary salinity but show minor proportions of secondary salinity and alkalinity. They are likewise high in chloride salinity but low in sulphate salinity. They are therefore primary waters, in which the alkali bases predominate and are of the nature of brines. Indeed in the synoptical table ocean water, characterized from Dittmar's analysis, falls just below water from the Brunswick well. To show this close relationship in quality the character outline of ocean water according to Dittmar's analysis is included in the table. The water of the Claremore well is also very similar in character to ocean water, although, of course, the waters of both the Claremore and the Brunswick wells are more dilute than sea water. The concentration or total reacting value of the border waters is nevertheless high as compared to that of the interior waters, which range from one-fourth to one-thirtieth that of the border wells. The interior wells are low in primary and secondary salinity but high in secondary alkalinity; chloride salinity is also low and sulphate salinity is a little higher. They are secondary waters, that is, they are waters in which the alkaline-earth bases predominate. Another difference not brought out in the table is that the waters of the border wells are charged with hydrogen sulphide, whereas the waters of the interior wells contain little, if any, of this gas.

These differences are directly attributable to the artesian circulation of the dome. When sediments are laid down upon the floor of the sea they are saturated with sea water, which remains in the pore spaces of the sediments as connate water until they are elevated into land, when it becomes a part of the circulating ground water. Diluted with atmospheric water, the salt is gradually carried away, and the ground water is "sweetened" and charged with elements dissolved from the sediments. This change proceeds, under favorable conditions, with sufficient rapidity to be detected by analyses made at long intervals. Examples of appreciable sweetening or freshening of salt waters have been noted[1] in the Atlantic Coastal Plain artesian belt.

As the Ozark artesian circulation developed and, with erosion of the Pennsylvanian shale, gradually extended itself down the slopes of the dome, the circulation in the rocks near the center was continually losing a portion of its chloride salinity and taking on secondary alkalinity (earthy carbonates), owing to dilution of the connate water and to solution of the country rock. This being so, we should expect that the water of wells near the center of the dome would show least chloride salinity and that of wells out in the Pennsylvanian shale area, beyond the border of the uplift, where the circulation beneath is practically impounded, would show the greatest chloride salinity, the water of the wells between showing degrees of chlorine salinity corresponding to the positions of the wells. And this, making allowance for local variations, is undoubtedly the case, as may be seen from the synoptical table (pp. 149–153). Of two deep wells at the same place, the shallower one should be expected to show less chloride salinity and otherwise to resemble the interior wells, owing to the greater volume of circulation in the shallower rocks as compared with the deeper rocks. The waters included in the table are arbitrarily chosen to bring out the results of the continued circulation and thus represent end series, between which all gradations may be found.

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[1] Sanford, Samuel, Saline artesian waters of the Atlantic Coastal Plain: U. S. Geol. Survey Water-Supply Paper 258, pp. 84–85, 1911.

SEGREGATION OF THE ZINC AND LEAD DEPOSITS OF THE JOPLIN REGION.

The stratigraphy, structure, and geologic history of the Ozark uplift have been described in some detail on the foregoing pages. The development of the underground-water circulation of the area, the quality of the water and its identical similarity to the solutions depositing the ores, the metalliferous content of the rocks, and the chemistry of lead and zinc solutions have been discussed, and also the effective modes of solution, transportation, and deposition of the metals. The segregation of the zinc and lead deposits of the Joplin region, as the writer conceives it to have taken place, may now be outlined by proceeding from the fundamental geologic facts here recapitulated to what seem to be reasonable and inevitable conclusions.

Conditions in Paleozoic time.—The Ozark region in its earlier period of development was centered about a crystalline pre-Cambrian archipelago, now represented by the St. Francis Mountains and outlying areas of crystalline rocks. On the sea bottom, which sloped gently away from this center on all sides, were laid down the sediments that formed the series of dolomitic limestones and minor amounts of sandstone and shale of the Cambrian and Ordovician rocks, the material composing which was derived from the crystalline areas by disintegration and solution, supplemented by deposition from material already in solution in the sea. During the Silurian and Devonian periods sedimentation was at times interrupted, or rather it was meager and local. In early Carboniferous time were laid down the sediments that formed the series of calcareous shales, cherts, and limestones constituting the Mississippian rocks. At the close of Mississippian deposition the land was elevated sufficiently to allow the development of a typical karst topography over much of the Ozark area. A general subsidence followed, and upon this karst surface Pennsylvanian shale was laid down over most if not all of the dome.

Presence of zinc, lead, and copper in the rocks of the Ozark region.—The large-quantity analyses made by Robertson demonstrate the widespread dissemination of minute quantities of zinc, lead, and copper in the crystalline rocks of the St. Francis Mountains, in the Cambrian and Ordovician dolomites, and in the Mississippian limestones. In the Cambrian and Ordovician systems zinc is the predominant metal, as is shown by Robertson's analyses, which are summarized on page 78. In the Mississippian limestones, according to the analyses on page 79, the quantity of lead, and even of copper, is greater than that of zinc, though the smaller quantity of zinc may be due in part to leaching during the post-Mississippian time, when the karst topography was being formed.

Though iron is not shown in the analyses we may be quite sure that it constitutes a larger proportion of all these rocks than do lead, zinc, or copper.

Selective solution of the metals in the crystalline rocks.—Gottschalk and Buehler have shown (see pp. 44–46) that the sulphides of the metals exhibit differences of electric potential and have tabulated them in an electrochemical series, with sphalerite, which has the lowest potential, at the bottom, and with galena, pyrite, chalcopyrite, and marcasite higher up in the series, in the order named. Arranged in pairs, in moistened contact, these minerals form batteries in which the sulphide having the lowest potential is dissolved while the other is practically unaffected. Thus sphalerite goes into solution in contact with galena, pyrite, chalcopyrite, and marcasite; and galena goes into solution in contact with pyrite, chalcopyrite, and marcasite. Furthermore, the lower sulphide goes into solution much faster when so coupled than when alone, sphalerite when coupled with pyrite dissolving 10 to 14 times as fast as when alone, and galena when coupled with pyrite dissolving 6 to 14 times as fast as when alone. As the metallic sulphides are finely disseminated through the crystalline rocks of the Ozark nucleus, innumerable particles of different sulphides must adjoin one another in the ground water, which will oxidize and dissolve the sulphides lowest in the scale first and those highest in the scale last. The order in which sulphide particles not in contact with other sulphides will go into solution will be determined by the rate of their solubility. The net result of the processes involved will be that the zinc sulphide will dissolve faster than the lead sulphide and that the sulphides of copper, iron, nickel, and cobalt will pass into solution more slowly than the sulphides of lead or zinc.

Selective precipitation of the metals in disseminated condition in the limestones forming on the sea floor.—When carried out to sea the metals will tend to be precipitated in the reverse order of their solubility, the less soluble nearer the shore, the more soluble farther out. The first sediments derived from the Ozark nucleus should therefore contain disseminated deposits of sulphides of zinc and of lead, lead in greater abundance near shore and the zinc in greater abundance farther out. So, too, later sediments—that is, sediments of a later geologic period—derived from the same nucleus, should contain disseminated sulphide of lead, relatively less abundant sulphide of zinc, and more abundant sulphides of iron and copper.

In accord with this general conclusion Robertson's analyses show that the Cambrian and Ordovician dolomites contain, on the average, nearly half as much zinc as the crystalline rocks, though they contain less than one-fourth as much lead and less than one-sixth as much copper. The Mississippian limestones, on the other hand, contain, on the average, about one-ninth as much zinc as the crystalline rocks but almost one-fourth as much lead and over one-third as much copper. By comparing the metal content of the Cambrian and Ordovician dolomites with that of the Mississippian limestones we find that, though the limestones contain, on the average, less than one-fourth as much zinc as the dolomites, they contain 30 per cent more lead and nearly twice as much copper.

Evidence of the very general presence of copper, lead, and zinc in sediments of all classes, including pelagic deposits has been given, and reasons for believing that these have been formed in part by chemical precipitation in the ocean have been presented. It is therefore believed that a part of the metals that are disseminated through the Cambrian and Ordovician dolomites of the Ozark uplift were derived directly from the ocean and that this portion is additional to the metals derived from the crystalline rocks of the St. Francis Mountains.

Uplift near close of Paleozoic time.—During the general orogenic and epeirogenic movement that occurred near the close of the Carboniferous period the Ozark uplift assumed practically its present outline and its quaquaversal arrangement, its structural culmination practically coinciding with the present areal and hydrographic center, which is about 100 miles west-southwest of the St. Francis Mountains, its center in early Paleozoic time. The St. Francis Mountain region still maintained a quaquaversal structure, however, though the elevated region was reduced in area on its western side.

Erosion of Pennsylvanian shale and establishment of artesian circulation.—When the cover of Pennsylvanian shale had been eroded from the central part of the dome an artesian circulation of the ground water was necessarily set up, and this circulation extended itself radially down the sides of the dome, the receiving area becoming larger as the inner edge of the shale retreated outward from the center of the dome.

Character of the ground water of the region.—We may get some idea of the quality of this circulating ground water from analyses of the waters of deep wells in the Ozark uplift, but a truer conception of its character may be gained from analyses of waters of deep wells in the Pennsylvanian area adjoining the uplift on the northwest. The wells in the Pennsylvanian area draw their supply from beds at the same geologic horizons as the beds that furnish water to the wells in the uplift, but, as in that area upward circulation has been greatly impeded or prevented by the cover of Pennsylvanian shale, the water has been to that extent impounded and is therefore more nearly like the original connate water, not having been freshened by continuous circulation in the manner already described. The analyses show that these deep-well waters are alkaline-saline and carry an excess of carbon dioxide, together with hydrogen sulphide.

Alkaline-saline sulphureted solutions containing an excess of carbon dioxide are effective in dissolving the sulphides, as is shown by the experimental work of Sullivan, and particularly by the work of Wells, with solutions of that character and as is further shown by the common presence of the metals as traces or measurable quantities in waters of that kind in Kentucky, in the Ozark region, in Colorado, and elsewhere. The underground water of the Ozark dome was (and is yet in lesser degree) alkaline-saline and is charged with sulphureted hydrogen and carbon dioxide, and it contains small quantities of zinc, lead, copper, and iron and minute traces of several other metals, as is shown by numerous analyses of deep-well waters from Missouri, Kansas, and Oklahoma (pp. 124–140).

Selective solution of the metallic sulphides disseminated in the dolomites and limestones of the central Ozark region and their transportation and segregation by the waters of the artesian circulation.—The Cambrian and Ordovician dolomites of the central area, having been laid down at a distance of 100 miles or so from the crystalline nucleus, should contain larger proportions of zinc than of lead, copper, or iron. In the solution and transportation of these metallic sulphides, selective solution of the sulphides, as determined by Gottschalk and Buehler, should have been effective, and we should find that relatively more zinc has been dissolved and also that it has been carried farther down the dome, and that relatively less lead has been dissolved and that it has been deposited sooner—that is, nearer the center of the dome. The long-continued operation of this process would bring about an arrangement of the sulphides with relation to the center of the uplift in which the ore deposits nearer the center would consist prevailingly of lead and those nearer the border would consist prevailingly of zinc. Correlatively copper and iron should be found nearer the center than lead. Such an arrangement is in fact found, as will be shown later (pp. 173–178).

When the water in its outward journey down the slope of the dome rose under artesian pressure to the surface at the inner margin of the Pennsylvanian shale, or perhaps under the edge of the Pennsylvanian shale, it came into the "open ground," due to the karst topography upon which the Pennsylvanian was laid down. Here, through release of pressure, carbon dioxide escaped from the water, and by its action, possibly aided by the lowering of the temperature and by decomposition of the carbonaceous matter of the shales, the metals were precipitated as sulphides through reactions with the hydrogen sulphide in the water, just as the metallic sulphides are precipitated to-day in containers holding samples of the deep-well waters and in the reservoirs supplied from deep wells.

Summary.—It is therefore held that artesian circulating alkaline-saline sulphureted waters, similar to those now rising in the deep wells west of the Joplin district, dissolved the disseminated zinc and lead, for the most part from the Cambrian and Ordovician rocks but in some part also from the Mississippian rocks, and transported these metals, in the form of bicarbonates, to their present position in the open ground which formerly lay at the base of the Pennsylvanian shales, and there deposited them as sulphides by reaction with the hydrogen sulphide of the waters on the escape of excess carbon dioxide. The chemical reactions here indicated are held to be the simplest and the most effective in segregating the Joplin ores, but it is not maintained that they operated to the exclusion of the other reactions set forth in the preceding pages. On the contrary many, if not all, of the reactions indicated in the chapter on chemistry should be considered in attempting to comprehend the work of a complex solution like the underground water of the Ozark dome.

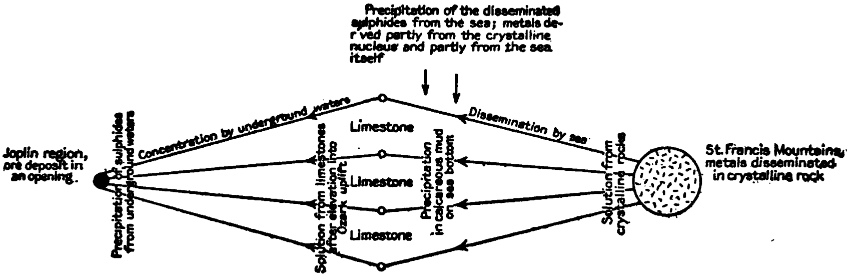
Precipitation of the disseminated sulphides from the sea; metals derived partly from the crystalline nucleus and partly from the sea itself
Joplin region, ore deposit in an opening.
Precipitation of sulphides from underground waters
Concentration by underground waters
Solution from limestones after elevation into Ozark uplift
Limestone
Limestone
Limestone
Precipitation in calcareous mud on sea bottom
Dissemination by sea
Solution from crystalline rocks
St. Francis Mountains, metals disseminated in crystalline rock

FIGURE 7.—Diagram to illustrate solution of metals from the crystalline rocks, their dissemination in the sea, their precipitation in disseminated form in the limestones, their solution in the underground waters after the elevation of the Ozark uplift, and their concentration and precipitation as ore deposits in openings in the rocks of the Joplin region.

The views presented in the foregoing outline of the segregation of the zinc and lead deposits of the Joplin district are essentially identical with the views of Van Hise, Bain, and W. S. Tangier Smith, and in respect to minimizing the extent of downward enrichment are also practically in accord with the views of W. S. Tangier Smith; but the writer assumes responsibility for the expression of the character of the circulating water and the discussion of the chemistry of the transportation and deposition of the metals.

The diagram shown in figure 7 is an attempt to trace graphically the progress of the metals from their original sources to their present location in the ore deposits of the Joplin region.

REVIEW OF COLLATERAL CORROBORATIVE EVIDENCE.

ITEMS OF THE EVIDENCE.

In formulating the theory of the genesis of the zinc and lead deposits of the Joplin district, outlined in the foregoing pages, the writer has collected various kinds of collateral corroborative evidence, the most important being the fact that sediments in reservoirs supplied by wells reaching the Ordovician and Cambrian rocks contain considerable quantities of metallic sulphides. The details of this evidence, as well as some pertinent deductions from the relative proportions of the different sulphides found, are given below. Other corroborative evidence includes the occurrence of dolomite with the ores, though the country rock consists of cherts and nonmagnesian limestone; the absence of ore deposits where the Chattanooga shale is known to be continuous; the distribution of the ore deposits in a circle about the Ozark uplift just inside of the margin of the Pennsylvanian shale; the distribution of the sulphides about the crystalline nucleus and about the structural center of the uplift, in harmony with the data concerning the solubility of the sulphides presented by Gottschalk and Buehler; the occurrence of bitumen at the base of the Pennsylvanian shale; the constant inflow of mine water at places where surface waters do not have access to the mine workings; and the geographic associations of the lead and zinc deposits of the eastern half of the United States with geanticlines and structural slopes. The details of the foregoing as well as other evidence are given in the following pages.

RESERVOIR SEDIMENTS.

RESULTS OF ANALYSES.

Many chemists who have experimented with alkaline-saline sulphureted waters similar to the deeper artesian waters of the Joplin district know that the heavy metals in such solutions are precipitated as sulphides after the water has been standing for some time and accumulate in the sediment at the bottom of the container. Robert Peter, A. M. Peter, and E. H. Keiser have chronicled this fact, as has been noted on pages 54 and 100.

Analyses of the deeper artesian waters of the Pennsylvanian area adjacent to the Joplin region show that they are alkaline-saline sulphur waters and shows also the fairly general occurrence in those waters of the metals, in particular of zinc, as traces or, more rarely, in weighable quantities. In many places these waters are used as the source of municipal supply, being stored in tanks or reservoirs. The sediments in such a reservoir accumulate until it becomes necessary for sanitary reasons to clean the reservoir. These reservoirs thus offer ideal conditions for the precipitation of the metalliferous content of the waters as sulphides, in the way in which the metallic sulphides are precipitated in the containers of water samples. The detection of a "trace" or even of a fraction of a part per million of zinc in a natural water may require a chemical test so refined or delicate that the result may be subject to more or less doubt. The accumulation of the metallic sulphides in reservoir sediments should probably not only provide sufficient material to set at rest any doubts about the occurrence of zinc in the water but should also afford material for determining the relative proportions of other metals which do not occur in the waters in quantities sufficient to indicate their presence on analysis, even as a "trace."

At first a few samples of reservoir sediment were obtained from reservoirs supplied by deep wells whose waters, unquestionably zinc bearing, as shown by tests, are derived from the Cambrian and Ordovician rocks. Analyses of these sediments disclosed such an interesting content of zinc, lead, copper, and iron sulphides that an attempt was then made to obtain samples from a considerable number of reservoirs supplied by deep wells drawing their water from the Cambrian and Ordovician rocks. Most of these reservoirs are in the Pennsylvanian shale area, in Missouri, Kansas, and Oklahoma, adjacent to the margin of the Ozark uplift, but a few of them are in the area underlain by the Mississippian limestones, within the border of the Ozark uplift. The following table gives 21 analyses of sediment from 14 reservoirs, with explanatory notes:

Determinations of zinc and other metals in waters of springs and deep wells and in sediments in reservoirs.

		Water.				Sediment (results expressed in percentage of total dried residue).											
										Ratio of zinc to—							
		No.[a]	Depth of well (feet).	Zinc (parts per million).	Analyst.	Zinc.	Lead.	Copper.	Iron.	Lead.	Copper.	Iron.	Sulphur.	Lime and magnesia.	Insoluble carbonaceous matter.	Insoluble silica and silicates.	Analyst.
1	St. Louis, Mo	56	2,199	......	......	0	0	0	35.65	......	......	......	......	([b])	......	......	Waring.
2	St. Peters, Mo	55	1,100+	......	......	0	0	0	2.38	......	......	......	0.463	6.85	Heavy.	68.28	Do.
3	Fulton, Mo	86	785	......	......	0	0	0	4.63	......	......	......	.031	32.27	Heavy.	13.64	Do.
4	.....do	86	960	......	......	0.220	0	0.049	1.50	......	1:0.223	1:6.8	......	53.46	0.35	0.47	Do.
5	Clinton, Mo	32	800	......	......	.165	0.0182	.0003	3.53	1:0.110	1:0.002	1:21.3	......	......	65.51		Do.
6	Neosho, Mo	......	292	......	......	.614	.004	0	......	1:0.007	......	......	......	......	7.88	77.18	Do.
7	Lanagan, Mo	......	435	......	......	.048	.036	.018	3.58	1:0.750	1:0.375	1:74.6	.93	......	3.41	78.91	Do.
8	Pittsburg, Kans	103	1,420	0.44	Palmer	.405	......	......	7.72	1:0.090	1:0.110	1:18.1	......	......	......	......	Palmer.
9	.....do	103	1,420	.60	Bailey	.074	......	......	......				......	......	......	......	Do.
10	.....do	103	1,420	......	......	4.4628	.1196	.1837	1.739				16.20	1.349	70.7	1.35	Waring.
11	.....do	103	1,420	Trace.	Waring	.1154	.008	.022	2.93				......	18.42	......	......	Do.
12	.....do	103	1,420	......	......	.0811	.014	.008	2.22				......	2.75	......	......	Do.
13	Columbus, Kans	5	1,400	Trace.	Bailey	.246	.035	.124	13.05	1:0.432	1:1.756	1:382.9	15.89	3.00	2.64	46.06	Do.
14	.....do	5	1,400	......	......	.034	.034	.094	26.61				40.64	2.39	11.07	19.12	Do.
15	.....do	5	1,400	......	......	.103	.016	.206	32.24				39.29	4.84	......	4.34	Do.
16	Afton, Okla	23	1,066	......	......	.0955	.0002	.0055	5.99	1:0.002	1:0.058	1:62.7	......	......	62.25		Do.
17	Vinita, Okla	15	665	Trace.	Palmer	.080	.026	.004	4.56	1:0.325	1:0.050	1:57.0	2.44	([b])	......	50.88	Do.
18	Pryor Creek, Okla	25	600	1.5	Waring	.231	.014	0	1.36	1:0.061	......	1:5.9	2.5	9.21	......	68.00	Do.
19	Claremore, Okla	45	1,035	Trace. .75	Keiser Palmer	.080	.006	Trace.	......	1:0.075	......	......	......	Large.	3.97	14.62	Do.
20	White Sulphur Spring, Ark	35	6	......	......	.388	.040	.005	2.10	1:0.256	1:0.098	1:69.5	1.45	21.34	......	49.93	Do.
21	Black Sulphur Spring, Ark	72	6	......	......	.022	.009	.004	2.94				2.82	1.40	......	49.82	
	Average ratios of the metals	......	......	......	......	......	......	......	......	1:0.211	1:0.334	1:77.6	......	......	......	......	

[a] Number of the analysis in synoptical table and table of analyses.

[b] Considerable.

1. The Belcher well (2,199 feet deep) is at Main and O'Fallon streets, St. Louis, Mo., but the water is carried three-quarters of a mile to the Belcher Hotel and bathhouse. The sediment was collected from the steel supply tank at the bathhouse. The well starts in Mississippian rocks and ends in Cambrian rocks.

2. The Silver well is 2 miles north of St. Peters, St. Charles County, Mo. The well is cased to 1,100 feet, one flow coming above that depth and the other from between 1,100 feet and the bottom of the well. The sample of sediment was scraped from the drain leading away from the well.

3. The Fulton [Mo.] Waterworks is supplied by two deep wells, the deeper one (785 feet) passing through 120 feet of Recent and Pennsylvanian rocks and reaching the Gasconade (Cambrian) formation. Sample of sediment collected from the very scanty deposit in the waterworks reservoir.

4. Sample of calcareous scale from a pipe at the State Hospital at Fulton, Mo., deposited by water from a well 960 feet deep, probably reaching the same horizon as the deepest well at the waterworks.

5. The Clinton [Mo.] Light & Water Co. utilizes the flow from several artesian wells, which penetrate 40 feet of Pennsylvanian shale and end in the Gasconade (Cambrian) formation at a depth of 800 feet. The sample of sediment is from a point near the inlet where the water enters the open reservoir.

6. The well at the United States fish hatchery near Neosho, Mo., is 292 feet deep, starting in the Mississippian rocks, passing through 22 feet of Chattanooga (Devonian) shale, and ending in Ordovician rocks. The water has a slight odor of sulphureted hydrogen, but no analysis is available. The sample of sediment was taken from the small basin about the mouth of the well, which barely flows at the surface.

7. The Walker well, near Lanagan, Mo., is 435 feet deep. The rock at the surface is shale belonging near the top of the Chattanooga (Devonian) shale. The water therefore probably comes from Ordovician rocks. It is highly charged with sulphureted hydrogen. The sample of sediment was collected from a wooden tank into which the well flows.

8–12. The municipal water supply of Pittsburg, Kans., is drawn from three wells, each about 1,420 feet deep, and, respectively, 6, 8, and 16 inches in diameter. The water rises in the wells to within 150 feet of the surface. The water from the 16-inch well is pumped into a round reservoir 80 feet in diameter, and the water from the other wells into a rectangular reservoir measuring 158 feet long, 90 feet wide, and 13 feet deep; both reservoirs are walled with brick and lined with cement. The two reservoirs are connected by a 6-inch pipe, and all water is drawn from the large rectangular reservoir. At a depth of 130 feet there is an underground chamber connected with the surface by two shafts, and the water from one of the wells is pumped into this reservoir by an air lift and then raised to the surface reservoir by a lift pump. Sample 8 came from the square reservoir near the supply pipe and 9 from a point 100 feet from the supply pipe. Sample 10 was obtained from the discharge pipe of the underground reservoir. Samples 11 and 12 came from the round reservoir, 11 from a point near the supply pipe and 12 from a point 50 feet away. The wells penetrate 250 feet of Pennsylvanian (Cherokee) shale and reach the Ordovician rocks at 621 feet, drawing their water supply from rocks of that age or older.

13–15. The municipal water supply of Columbus, Kans., is drawn from a well 1,400 feet deep, which passes through 165 feet of the Cherokee shale and through the Mississippian rocks and draws its supply from the Ordovician and Cambrian rocks. From the well the water, which rises within 65 feet of the surface, is pumped to a surface-aerating reservoir and thence to the stand tower. The samples of sediment were collected from the cement surface reservoir.

16. The water supply at Afton, Okla., is derived from two wells, each 1,066 feet deep, which pass through the Mississippian rocks and the Chattanooga (Devonian) shale and draw their supply from the Ordovician and Cambrian rocks. The eastern

margin of the Cherokee shale (Pennsylvanian) is about a mile west of the well. The water rises above the ground to a height of 3 feet and pours out into a cemented basin, from which it is lifted by pumps to a stand tower. The samples of sediment were collected from the basin.

17. The municipal water supply of Vinita, Okla., is derived from several flowing wells, which draw their chief supply from a water sand at a depth of 665 feet and smaller supplies from a sand at a depth of 510 feet, both of which are in the Ordovician. The wells pass through 95 to 100 feet of Cherokee (Pennsylvanian) shale in their upper portion. The water flows from the wells into a square cement-lined reservoir, from which it is pumped into the stand tower. The sample of sediment was collected from the bottom of the reservoir.

18. Whitaker Park, at Pryor Creek, Okla., utilizes the artesian flow of a well 600 feet deep that draws its supply of water from the Ordovician rocks, which lie beneath the Mississippian limestones and 140 feet of Pennsylvanian shale. The sediment was collected from a wooden trough leading from the well.

19. At Claremore, Okla., there are three deep wells near together, which range in depth from 1,100 to 1,500 feet. The wells pass through 750 feet of shales and sandstones of Pennsylvanian age, and then through 280 feet of Mississippian rocks, reaching 40 feet of Chattanooga (Devonian) shale at 1,035 feet, beneath which, in the Ordovician rocks, the artesian flows are found. The sample of sediment was collected from a wooden tank in the bathhouse of the Radium Water Sanitarium Co. after having been piped 80 feet from the Brown well.

20-21. At Sulphur Springs, Ark., there are several springs in a small park in the valley of Butler Creek. The basins of these springs are about 6 feet deep and the water emerges from Ordovician dolomitic limestones. The Chattanooga (Devonian) shale outcrops on the hillside about 50 feet above the level of the springs. The samples of sediment were collected from the bottoms of the spring basins. The water at the springs has a distinct odor of hydrogen sulphide.

PHYSICAL STATE OF THE TRANSPORTED METALS.

SUSPENDED OR COLLOIDAL PARTICLES.

At the outset it will be well to consider the possibility that the metals deposited with the reservoir sediments may have been transported in the waters as sulphides in fine or colloidal suspension or blown into the reservoirs as dust by the wind.

The waters are derived from the Cambrian and Ordovician rocks and (as is shown on p. 250) must have traveled an average of more than 60 miles from intake to well. It would probably require 50,000 or 100,000 years to make the journey, a period that would apparently be long enough to permit the suspended particles to subside. Moreover, it is difficult to see how the fine metallic sulphides could be continuously freed from the Cambrian and Ordovician rocks with sufficient regularity to yield year after year the quantity that is deposited in the reservoirs, or, by an extension of the reasoning to geologic time, to give rise to the ore deposits of the district.

If the suspended particles be supposed to originate from the well bore, it does not seem reasonable that they should be detached in about the same quantities in different wells, or in the same well at different times, or that the supply should continue indefinitely. So far as known to the writer, no traces of zinc or lead deposits were reported in the logs of any of the wells delivering water to the reservoirs from which sediments have been analyzed.

If the suspended particles be supposed to be in a colloidal condition, the precipitating effect of electrolytes in the deep waters must be taken into account. The waters of some of the wells, as, for instance, the Whitaker Park well at Pryor Creek and the Radium well at Claremore, contain rather high percentages of sodium chloride—are, in fact, unpalatably strong brines—yet these waters carry a particularly high content of zinc, that of the water of the Pryor Creek well having been determined by Prof. Waring as 1½ parts per million. Clark[1] found that carbon dioxide and hydrogen sulphide increased the amount of colloidal copper sulphide held in suspension in water and in a $\frac{1}{300}$ normal solution[2] of sodium chloride or potassium chloride. The water of the Whitaker well contains sodium chloride equivalent to a 6-fold normal solution, and that of the Radium well is equal to a 30-fold normal solution, that is, from 1,800 to 9,000 times as strong as the solution in Clark's experiment. In the early part of the period of ore deposition, when the artesian circulation had not been long established, the underground water must have consisted largely of the connate water of the rocks and must generally have approached sea water in chloride salinity, approximately a 27-fold normal solution.

All electrolytes precipitate colloids when both are in sufficient concentration, but the "precipitating power of electrolytes increases decidedly with the valence of the precipitating ions (H. Schulze's rule). Bivalent ions are far more efficient than univalent; trivalent ions in turn are still more effective than bivalent." [3] In addition to sodium chloride most of the deep waters contain calcium chloride, calcium carbonate, magnesium chloride, magnesium carbonate, alumina, and ferric oxide. These are all effective flocculents and precipitants of colloids, and in accordance with the rule, alumina and ferric oxide are particularly effective. Corroborative results on colloidal copper sulphide by the use of calcium chloride, calcium carbonate, and alumina were obtained by Clark,[4] who also found that carbon dioxide, of which there is always more or less in the deep waters, "caused a very clean-cut flocculation of the colloidal copper sulphide" in the presence of a very dilute ($\frac{1}{1400}$ normal) solution of potassium carbonate and potassium chloride.

In the face of these facts any supposition that the metals are carried in suspension would seem to the writer to be untenable.

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[1] Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., vol. 1, No. 2, p. 139, 1914.

[2] A normal solution is one in which 1 gram of the substance is dissolved in 1 liter of the solution.

[3] Stieglitz, Julius, The elements of qualitative chemical analysis, vol. 1, p. 135, 1912.

[4] Clark, J. D., op. cit., pp. 137-141.

WIND-BLOWN PARTICLES.

As most of the samples of sediment from Kansas and Oklahoma were taken from open waterworks reservoirs, some of which were near railroads that may have been carrying concentrates to Kansas and Oklahoma zinc smelters and most of which contained a great deal of wind-blown material, it is advisable to consider the possibility that the zinc in the sediments was carried there by wind. The zinc may have been so carried into the water in three conceivable forms: (1) As fume from zinc smelters; (2) as dust particles from the soil; (3) as fine particles of zinc-blende concentrate blown from loaded cars in transit.

1. There are two zinc smelters in the vicinity of Pittsburg, Kans., but they are, respectively, 1 mile north and 2 miles northeast of the reservoirs from which the sediments were taken. The prevailing winds are from the southwest and would carry any fume in the opposite direction from the reservoirs. Moreover, the smelters were not in operation during any part of the year that the sediments were accumulating. The sample that shows the highest zinc content (sample No. 10 in the table on p. 164) was collected in the discharge pipe from the underground reservoir, where it could not have received any additions of atmospheric dust. Finally, samples of water collected directly from these and other wells contain measurable quantities of zinc, as is shown in the table on page 164. None of the other samples was taken from reservoirs anywhere near a zinc smelter.

2. The sediments taken from the open reservoirs invariably yield the metals as amorphous sulphides, except only some crystallized pyrite. The metals found in sediments deposited in samples of water drawn directly from the wells also occur in the form of amorphous sulphides. If the metals were derived from wind-blown dusts carried from the soil they would probably occur in some oxidized form. The percentage of the metals in the sediments is much higher than that which the soils would be likely to contain over the wide area covered by the samples of sediment collected, and it seems improbable that the heavy metals would be concentrated in a wind-borne deposit. The sediment from the Fulton Insane Asylum was an incrustation from the boiler-water heater and came directly from the well without exposure to the air. The same is true of a sample from Pryor Creek, which contained zinc, but which was discarded in favor of a sample taken later from the trough leading away from the well. The sample from Claremore was taken from a closed tank inside the building and had not been exposed to the open air. Finally, the sediment from the Fulton reservoir and that from a ditch leading from the Silver well showed neither zinc nor lead, although these places are easily accessible to dust-laden winds.

3. The average of nine composite analyses, covering 45,000 shipments of zinc concentrates, mostly carload lots, made between 1900 and 1913, is as follows:

Average metal content of 45,000 shipments of zinc concentrates.

	Per cent.
Zinc	57.507
Lead	.939
Copper	.044
Iron	2.335

In the following table the other metals in the concentrates are reduced to their ratio to zinc in order that they may be compared with the similar average ratios of the metals in the sediments:

Ratios of zinc to other metals in reservoir sediments and in zinc concentrates.

	Ratios.		
	Zinc to lead.	Zinc to copper.	Zinc to iron.
In reservoir sediment	1:0.211	1:0.334	1:77.6
In 45,000 shipments of zinc concentrates	1:0.16	1:0.0008	1:0.041

Zinc concentrates are shipped from Joplin northwestward and southwestward to smelters in Kansas and Oklahoma, but no lead concentrates are shipped in those directions. Many of the reservoirs from which samples of sediment were obtained are from a quarter of a mile to a mile from a railroad, over which possibly no zinc concentrates have ever been shipped. But under the most favorable assumptions the metals of the sediments can not have been derived from wind-blown zinc concentrates for the reason that the sediments contain proportionately an average of 13 times as much lead, more than 400 times as much copper, and nearly 1,900 times as much iron as do the zinc concentrates.

DEDUCTIONS FROM ANALYSES SHOWING METALLIC CONTENT AND RATIOS OF THE METALS IN ROCKS, RESERVOIR SEDIMENTS, AND ORES.

Important deductions may be drawn from the determined ratio to one another of the several metals contained in the sediments. In order that the ratio to each other of some pair that occurs in large proportions in certain sediments may not have undue weight in determining the average ratio, the ratios of the same pair of metals in sediments in which they occur in smaller quantities have been determined, and a common measure of ratio has been established by taking zinc as unity. The average ratios for the metals thus determined are therefore true averages.

It is interesting to compare the ratios of zinc to lead, copper, and iron in the reservoir sediments with the ratios of zinc to lead and copper in the large-quantity analyses of rocks by Robertson and by Weems, and with the ratio of zinc to lead, copper, and iron in the ores mined in the Joplin district from 1907 to 1913, inclusive. The results of Robertson's and of Weems's work have already been given. The ratio of zinc to lead in the concentrates as sold in the Joplin district may be obtained from the statistics of production of these metals given in the United States Geological Survey's annual volumes of "Mineral Resources of the United States" for the period indicated. The local record of sales made before that period does not distinguish between sulphide and oxidized ores of zinc and does not give the metal content of either, so that accurate comparison can be made only as far back as 1907. Assuming that lead and zinc are recovered from the crude ore of the district in equal proportion, the ratio of zinc to lead produced during the last seven years is as 1: 0.229. It is possible, however, that, owing to its higher specific gravity, galena in hydraulic concentration is recovered in a proportion greater than that of sphalerite, and if so, the ratio of zinc to lead given in the table on page 171 is not high enough. On the other hand, it is clear that a larger proportion of lead ore was raised in the early days than now, and that a larger proportion of oxidized zinc ores was raised then than now. This should be expressed by raising the ratio of lead to zinc, which would operate to offset the decrease just mentioned, so that perhaps the figure given for lead is not far from the actual figure. The average proportion of copper in zinc concentrates may be determined from available assays of composites of samples of several thousand carload lots.[1] Similarly an estimate of the copper in lead concentrates may be made from the determinations of Petraeus and Waring.[2] From these may be calculated the total copper contained in the zinc and lead concentrates produced in the last seven years and also the ratio of the zinc to the copper. From the same sources the iron contained in the concentrates may be computed, and from that the ratio of zinc to iron may be derived. This will take into consideration, however, neither the iron in the zinc concentrates from the Miami (Okla.) district, which carry a heavy content of iron and which are not included in the composite analyses, nor that in the zinc concentrates of other districts, which contain so much iron that they must be treated in a roasting magnetic-separation plant before being sold, nor the pyrite of the discarded middlings separated in concentrating the ores, nor further, the specially pyritiferous portions of mines which are avoided in mining. The iron is therefore too low. The copper occurs as chalcopyrite, which in concentration is drawn off with the pyrite middlings and discarded, so that it is not represented in the composite assays mentioned above. It therefore appears that the ratios of copper and iron to zinc must be considerably higher than the figures calculated. Both the ratio of zinc to copper and of zinc to iron are given in the table below, which includes also the ratio of zinc to lead, copper, and iron in the reservoir sediments and, for convenience, gives the results of Robertson's and of Weems's large-quantity analyses. (See pp. 78–79.)

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[1] U. S. Geol. Survey Mineral Resources, 1913, pp. 122–124, 1914.

[2] Petraeus, C. V., and Waring, W. G., Eng. and Min. Jour., vol. 80, p. 721, 1905.

Metallic content and ratios of the metals in rocks, reservoir sediments, and ores.

	Average percentages.			Ratios of metals.		
	Zinc.	Lead.	Copper.	Zinc to lead.	Zinc to copper.	Zinc to iron.
MISSOURI.						
Pre-Cambrian rocks	0.00901	0.00397	0.00590	1:0.440	1:0.653	....
Cambrian and Ordovician limestones	.00425	.00096	.00126	1:0.225	1:0.297	....
Mississippian limestones	.00104	.00115	.00202	1:1.107	1:1.817	....
IOWA.						
Ordovician and Silurian limestones	.00029	.00326	....	1:11.1	....	....
Cambrian and Ordovician limestones of Missouri	....	....	....	1:0.225	1:0.297	....
Reservoir sediments	....	....	....	1:0.211	1:0.334	1:77.6
Ore shipments, 1907–1913	....	....	....	1:0.229	1:0.0007	1:0.0412

From an inspection of the table it appears that the ratio of zinc to lead in the reservoir sediments agrees closely with that of zinc to lead in the Cambrian and Ordovician dolomites, from the artesian circulating water in which the sediments were derived. This agreement acquires significance when it is seen that the ratio in the Cambrian and Ordovician rocks differs widely from the ratio in the pre-Cambrian, from that in the Mississippian, and from that in the Ordovician and Silurian rocks of Iowa. The ratio of zinc to lead in the ores now being mined also agrees practically with the ratio in the sediments and in the Cambrian and Ordovician rocks. This accords with the theory here presented, that the metals of the ores and of the sediments were derived from the metals of the Cambrian and Ordovician dolomites. However, for reasons given above, too much stress should not be placed upon the figures showing the ratio of zinc to lead in the ores as mined.

The proportions of the other metals in these three substances, however, are decidedly different, but the differences are such as would be expected from a consideration of facts that have been heretofore presented. Gottschalk and Buehler have shown that, when in contact, sulphides of copper and iron lag behind sulphides of lead and zinc in going into solution. When the sulphides of these four metals are disseminated through rocks subjected to continuous leaching by circulating underground water the solution passing through in the earlier stages of the leaching will (zinc not considered) carry proportionately more lead, and in the later stages proportionately more copper and iron. Hence we see that the ores that represent an earlier stage of leaching contain a much smaller proportion of copper and iron to zinc than the original limestones. On the other hand, the sediments, which represent a later stage of leaching, contain ratios of copper and iron to zinc much larger than those in the ores or even, so far as copper is concerned, in the original limestones. Unfortunately, the analyses made by Robertson do not show the iron content of the rocks, so that the descent of the metal from the limestones to the sediments and ores can not be traced for iron, as it can for copper.

Copper occurs in the ores chiefly as chalcopyrite. The usual crystal form of this mineral is the tetrahedron, with parallel orientation, the crystals being formed on the surface of sphalerite, as shown in Plate VI, *B*, but it also occurs on dolomite and other minerals. Whatever its occurrence, it is always among the last minerals to be formed, a fact that supports the argument—drawn from Gottschalk and Buehler's order of solution in pairs, and from the composition of the reservoir sediments and of the ores—that copper was relatively more abundant in the later stages of the development of the ground-water circulation.

Iron occurs in the ores as marcasite and pyrite. These also are among the very last minerals to be deposited, a fact that corroborates the evidence furnished by the chalcopyrite as to the order of solution of the metals and their relative abundance in the sediments and in the ores and indicating the relatively greater abundance of iron in the later stages of the development of the circulation. The following quotation describes the paragenetic relations of the iron sulphides to the other ore and gangue minerals as noted by Smith:[1]

> Iron sulphide formed earlier than galena or sphalerite has not been noted. When occurring with these minerals, it is in all cases superposed on them, showing locally a preference for one or the other, especially galena. Both marcasite and pyrite have been seen on chalcopyrite, while minute crystals of pyrite have been noted on marcasite crystals. Where these sulphides occur as metasomatic replacements they appear to have been developed simultaneously. A second generation of marcasite is sometimes seen, and in one instance was noted as occurring in the surface layer of calcite crystals. At the Mildred mine, west of Joplin, chalcopyrite and marcasite crystals are covered with calcite crystals, which in turn show hemispherical and botryoidal marcasite on their surfaces. In a number of instances in the sheet ground about Webb City marcasite has been noted in corrosion cavities in galena.

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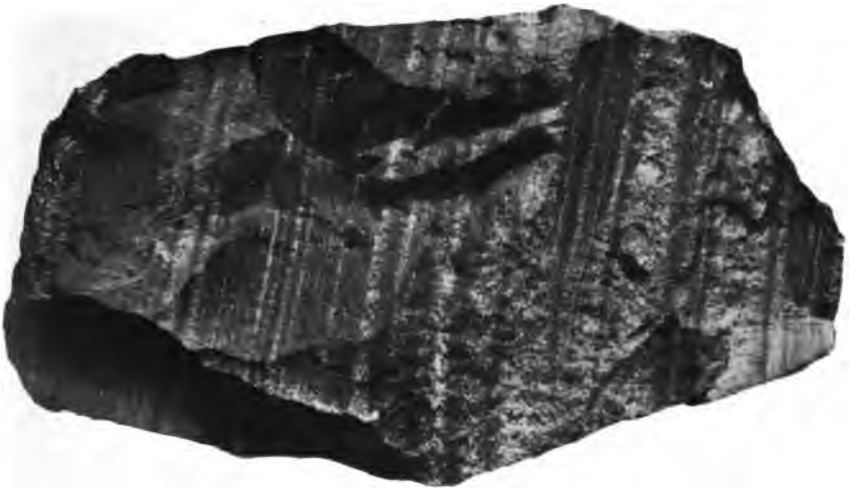
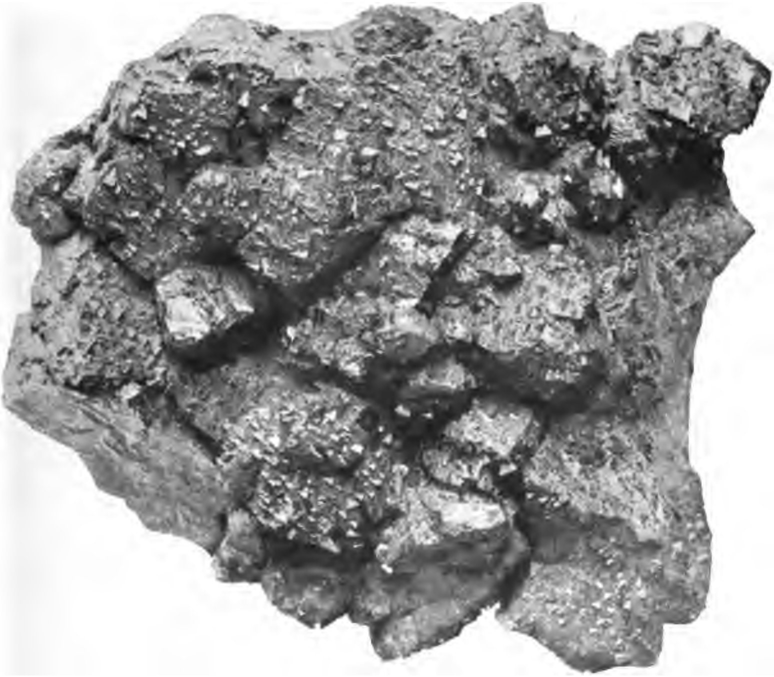
[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 13, 1907, reprinted 1914.



A. SPECIMEN OF JASPEROID SHOWING FINE BANDING.



B. SPECIMEN OF CRYSTALIZED CHALCOPYRITE WITH PARALLEL ORIENTATION ON SPHALERITE.

From cavity in sheet ground.

RATE OF DEPOSITION OF ZINC IN RESERVOIR SEDIMENTS.

When the reservoirs at Pittsburg, Kans., were cleaned out in April, 1911—about a year had passed since the last cleaning—the depth of the sediment in different parts of the reservoirs ranged from half an inch near the discharge pipe to a quarter of an inch at the far sides, averaging about three-eighths of an inch. When the area of the reservoirs was taken into consideration, it was found that the sediment which had collected in the course of a year amounted to 600 cubic feet, which contained 5½ pounds of zinc or 8¼ pounds of zinc sulphide. During the year in which the sediment collected there was supplied to the city of Pittsburg 385,000,000 gallons of water. The quantity of zinc precipitated in the sediment indicates that the zinc content of the water was 0.00173 of a part per million.

In two determinations of zinc in water from the Pittsburg wells, one made by E. H. S. Bailey, of Kansas State University, in 1897, and the other made by Chase Palmer, of the United States Geological Survey, in 1910, the zinc content was estimated as 0.6 and 0.44 of a part per million, respectively. If all the water pumped into the reservoir in a year averaged 0.5 of a part per million of zinc, the total zinc content would be 1,600 pounds, or nearly 2,400 pounds of zinc sulphide. Therefore, not all of the zinc is precipitated in the reservoir, but a large proportion of it goes out with the water pumped from the reservoir. Another portion is precipitated in the underground reservoir and is not represented in the sediments.

PLACE RELATIONS OF THE ZINC, LEAD, COPPER, IRON, NICKEL, AND COBALT DEPOSITS TO THE PRE-CAMBRIAN NUCLEUS AND TO THE POST-CARBONIFEROUS CENTER OF THE OZARK UPLIFT.

The interesting and important results of the work of Gottschalk and Buehler (see pp. 44–46) throw much light on the distribution of the ore minerals with relation to the pre-Cambrian nucleus and incidentally upon the genesis of the ores. As the metallic sulphides are finely disseminated through the crystalline rocks of the nucleus, innumerable particles of different sulphides must lie in contact with one another in the underground water, which will oxidize and dissolve the sulphide lowest in the scale first and the one highest in the scale last. The sulphide particles not lying in contact will go into solution in the order of their solubility. The net result of the processes involved will be that the zinc sulphide will dissolve faster than the lead sulphide, and that the sulphides of copper, iron, nickel, and cobalt dissolve more slowly than the sulphides of lead or zinc. The same principles that operate for adjoining sulphide particles will operate, only much more strongly, for the sulphide components of mixed sulphide ore bodies when they are subjected to leaching.

When carried out to sea the metals will tend to be precipitated in the reverse order of their solubility. The less soluble ones will be precipitated nearer shore and the more soluble ones will be carried farther out to sea. As the pre-Cambrian nucleus was the source of the metals in Cambrian and Ordovician time, we should naturally suppose that the metals carried out and deposited in the Cambrian and Ordovician sediments would be arranged in an order conforming to the principle set forth. That is to say, we should suppose that zinc especially, considerable lead, and some copper and iron would be carried far out to sea, and that a great deal of the lead, most of the copper, and most of the other metals, except zinc, would be deposited with the limestones laid down nearer the nucleus. As a matter of fact, these suppositions represent the distribution of the metals as they are found to-day. The mixed sulphides of nickel, cobalt, and copper are mined in connection with lead sulphide in Madison and St. Francois counties, Mo., on the eastern flank of the pre-Cambrian nucleus, and copper ore free from nickel and cobalt has been mined in Ste. Genevieve and Shannon counties, respectively, a short distance east and west of the nucleus. The heaviest iron deposits form a circle about the St. Francis Mountains except on the northeast. The largest deposits of lead connected with the Ozark uplift are found on the eastern flank of the nucleus, but considerable lead is found far from the nucleus, and the largest zinc deposits are in the Joplin region on the extreme western margin of the uplift.

Pošepný [1] notes this relation of the ores to the Archean nucleus and comments thereon as follows:

> The deposits occurring near the "islands" of granite and porphyry have special interest. While the Silurian limestones of the surrounding country, farther from these islands, present chiefly only lead and zinc ores, other metals, such as copper, cobalt, and nickel occur as the Archean foundation rocks are approached; and this circumstance is, to my mind, an indication that the source of the lead deposits also is to be sought in depth.

It may therefore be inferred that Pošepný believed that the metals have been drawn from depth in the Archean area, which then became the center of dispersion of the metals into the surrounding sediments, resulting in the relations noted.

In a recent report on the iron ores of Missouri Crane [2] finds that two classes of the ores, the secondary limonite and the hematite of the filled sinks were originally deposited in the form of the sulphides, as is shown by the fact, among others, that pseudomorphs after marcasite and pyrite, principally marcasite, are found. The hematite ores are those referred to as "the specular ores of the sandstone region" by Nason,[1] who believed that they were deposited as sulphides by descending waters. Crane holds further that the hematite ores of the filled sinks were deposited as sulphides by descending waters, which leached the metal from the overlying Pennsylvanian rocks, just as Buckley and Buehler held for the lead and zinc ores of the Ozark region. Crane and Nason as well as Bain[2] have noted the occurrence of lead, zinc, and copper sulphides and oxidized ores with the iron ores of the filled sinks.

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[1] Pošepný, Franz, The genesis of ore deposits: Am. Inst. Min. Eng. Trans., vol. 23, p. 303, 1894.

[2] Crane, G. W., The iron ores of Missouri: Missouri Bur. Geology and Mines, vol. 10, pp. 76–77, 98–105, 1912.

The present position of the iron ores that have been derived from sulphide deposits also harmonizes well with the artesian theory of origin, if the operation of the principle of selective solution of the sulphides set forth by Gottschalk and Buehler is taken into account. In the dissemination of the metals into the Cambrian and Ordovician seas from the crystalline rocks of the St. Francis Mountains the iron in contact with the other sulphides would have a tendency to hold back, but in fact, owing to its preponderance over the other metals, more iron would be disseminated than other metals. The principle of selective solution would apply again, and more particularly to the sulphide constituents of any ore bodies formed by early circulation in the quaquaversal pre-Silurian rocks about the crystalline nucleus. Here, with the mixed sulphides in contact, the iron and copper would lag behind the lead and zinc in solution, and after several decompositions and recompositions in its transfer down the slope a mixed sulphide ore body would practically be freed entirely of lead and zinc and finally of copper also, leaving iron alone. If now, through erosion, the iron sulphide body is brought near the surface it might be completely oxidized and rendered comparatively permanent in form and position. It will be noted that the heaviest iron deposits encircle the St. Francis Mountains, except to the northeast, as though their distribution had been controlled by that center.

The present distribution of the metals, however, has been complicated by elevations which took place at the close of Mississippian and Pennsylvanian time, respectively. These elevations, discussed more fully on page 32, shifted the culminating point of the uplift from the pre-Cambrian nucleus to the present center of the dome in the vicinity of Wright County, Mo., 100 miles west of the pre-Cambrian nucleus. The post-Mississippian elevations exposed to erosion the Mississippian and the Cambrian and Ordovician limestones, in which a karst topography was developed. The limestones of both these periods contained disseminated metals, as is shown by Robertson's large-quantity analyses. The Cambrian and Ordovician limestones, as already pointed out, contain lead and zinc in about the same proportions as the ores now mined in the Joplin district, but the Mississippian limestones contain a larger proportion of lead. This difference is perhaps to be explained by the greater exposure of the Mississippian rocks to erosion during the post-Mississippian elevation, the disseminated zinc content being more easily dissolved than the lead, which remained behind.

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[1] Nason, F. L., A report on the iron ores of Missouri: Missouri Geol. Survey, vol. 2, pp. 140-147, 1892.

[2] Bain, H. F., and Ulrich, E. O., The copper deposits of Missouri: U. S. Geol. Survey Bull. 267, p. 48, 1905.

After the deposition of the Pennsylvanian shales, the post-Carboniferous elevation resulted in the erosion of the Pennsylvanian and in the exposure of the Cambrian and Ordovician and the Mississippian limestones on the crest of the uplift. The initiation of a radial artesian circulation, with the crest of the dome as the receiving area, established a new center for the dispersion of the metallic contents of the rocks. The limestones of the central area, having been laid down at a distance of a hundred miles or so from the pre-Cambrian nucleus, probably contained a larger proportion of zinc than lead and very much smaller proportions of the other metals. In the solution and transportation of these metallic sulphides the rule enunciated by Gottschalk and Buehler would again hold, and the ore deposits in the central area of the uplift should contain more lead and those farther down the dome should contain more zinc. This is found to be the fact, as shown below. The dispersion of iron from the new center is indicated by the ringlike arrangement of the scattered iron deposits about the center.

As the pre-Cambrian nucleus still retained its quaquaversal structure, the effect of the differential solution of the sulphides would be operative there also. The Cambrian dolomites adjoining the nucleus would be added to the crystalline rocks of the nucleus as a source of the metallic content of the circulating ground water. These limestones, we have seen, should be relatively rich in lead sulphide and the other sulphides that stand higher in the Gottschalk-Buehler scale, but should contain a relatively small proportion of zinc. Buckley[1] comments on the absence of zinc in the mine waters of the disseminated lead district of southeastern Missouri, though Robertson's large-quantity analyses show more zinc than galena in the pre-Cambrian crystalline rocks. Zinc can not be entirely absent from the water derived from the Lamotte sandstone, however, for a sample of the incrustation upon the screen of the outlet pipe at the reservoir of the waterworks at Bonneterre, Mo., the supply of which is drawn from the Lamotte sandstone, was analyzed with the results given below. The material was kindly furnished by Mr. O. M. Bilharz. The water in the reservoir comes in contact only with ordinary iron pipe.

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[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, vol. 9, p. 227 [1909].

triangles represent copper
es inclosed in circles repre-
:kel, and cobalt deposits.
.nt the zinc percentage of
ıt of lead and zinc in each
on. Solid circles represent
lized from sulphides
30 40 50 60 70 80 Miles
39°
39°
37°
37°
89°
LINOIS
K
SSISSI
River
Ohio
79
RIVER
KENTUCKY
TENNESSEE

Analysis of incrustation from waterworks reservoir at Bonneterre, Mo.

[W. George Waring, analyst.]

	Per cent.
$CaCO_3$	Large.
SiO_2	1.2
Fe	.72
Pb	.004
Zn	.0027
Ni and Co	No trace.

The material consists almost wholly of calcium carbonate.

Sphalerite has been found in recent years in the deeper workings of several of the lead mines of southeastern Missouri, the zinc content of the ore occasionally amounting to one-sixth as much as the lead content.

The accompanying map (Pl. VII) shows that the economic deposits of zinc, lead, copper, iron, nickel, and cobalt are distributed about the dome in relations precisely accordant with the data given by Gottschalk and Buehler. The copper, iron, nickel, and cobalt and the heavy lead deposits of the southeastern Missouri area are represented by conventional signs, but the proportion of zinc to lead in the total ores mined in each county is shown by the black-face figures on the map. These figures are based on statistics of production by counties as given by Winslow,[1] supplemented by statistics of county production for later years, given in the annual reports of the Missouri Bureau of Mines and Mine Inspection. Counties for which no figures are given on the map have no reported production. Counties marked "O" have been credited with production of lead but not of zinc. The line drawn through the counties which have produced about equal quantities of lead and zinc, leaving those with more than 50 per cent zinc on the outside and those with more than 50 per cent lead on the inside, is especially significant, because it incloses the two structural centers of dispersion of the metals and thus represents graphically the selective solution and precipitation of lead and zinc sulphides as related to the artesian circulation of the Ozark dome. Lead is dominant over zinc within the line, though it extends in quantity beyond to the Pennsylvanian shale border, but it will be noted that the iron deposits are very nearly limited to the area within the line, those deposits outside the line occurring in the territory immediately adjacent to it.

Indications of similar place relation of the ores to the intake of the artesian circulation are pointed out in the discussion of the origin of the ores of the Kentucky-Illinois fluorspar district (pp. 213–217).

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[1] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 507–538, 1894.

Referring to the lead and copper deposits of Wisconsin, Chamberlin says:[1]

> On pages 72 to 78 of the present volume [Geology of Wisconsin, vol. 4] Mr. Strong has reviewed more fully than any previous observer the facts at present ascertainable in relation to the occurrence of lead in the Lower Magnesian limestone of the region lying immediately north of what is recognized as the lead district proper, and to this [these pages] the reader is referred. On pages 69 to 72 he has described the copper deposits of the same region, which should be studied in connection with the lead, since they belong to the same class of deposits and occur in essentially similar situations. * * *
>
> On pages 69 to 72 of this volume Mr. Strong describes the copper deposits of this formation found in the metalliferous area immediately north of the lead region, from which it appears that this ore, though not attaining, so far as past developments have demonstrated, industrial importance, yet has a development altogether exceptional in the formation in which it is situated; for, although the Lower Magnesian limestone is fully developed and extensively exposed both to the westward and northwestward, eastward and northeastward from this region, it does not there present any noticeable traces of cupriferous ores. These localized deposits therefore fall in the same category with the ores that have formed the main subjects of our present discussion, and it is evident that this area is to be added to the heretofore recognized lead region, as forming one general mineral district. The force of this conclusion becomes more especially evident when we consider the fact that copper occurs at several localities in the heart of the lead region and that at Mineral Point, in particular, it develops mines of economic importance. * * *
>
> Its [copper's] comparative frequency in the Lower Magnesian limestone north of the lead region proper, where iron also abounds but zinc has not yet been found, may be regarded as lending support to the view that its distribution accords more closely with iron than zinc.

In a later paper Cox[2] makes the statement that copper ore to the value of more than $250,000 has been shipped from the vicinity of Mineral Point, on the eastern border of the district. He describes a copper prospect near Gratiot, southeast of Mineral Point, which gives indication of developing a considerable body of copper ore.

The rock strata in the upper Mississippi Valley district slope southward and westward, away from the Wisconsin uplift, and the artesian circulating water must flow in the same direction. The occurrence of deposits of galena, pyrite, and copper to the north, northeast, and east, up the slope from the main deposits of lead and zinc ores thus accords strictly with the place relation of similar ores to the Ozark uplift.

ASSOCIATION OF THE ORES WITH DOLOMITE AND JASPEROID.

RELATIONS OF THE METALS TO THE GANGUE MINERALS.

The principal nonmetallic minerals and rocks associated with the ore deposits of the district are dolomite, calcite, secondary limestone, and jasperoid, a dark siliceous rock resembling chert, called cherokite

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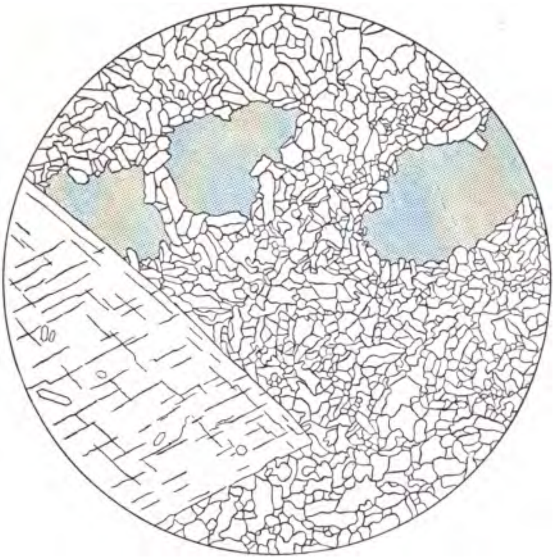
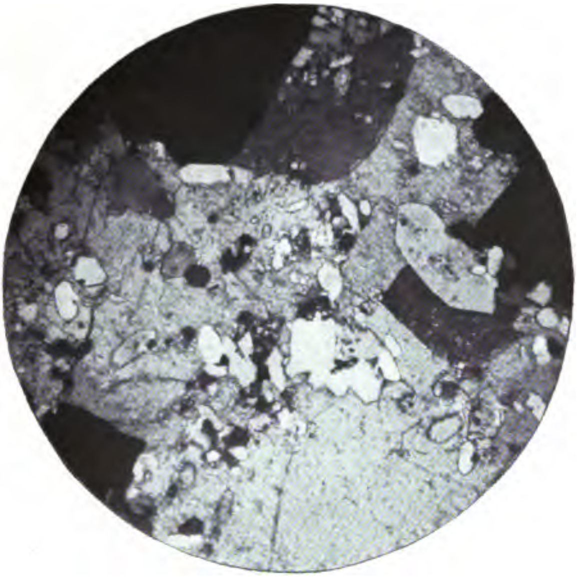
[1] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geology of Wisconsin, vol. 4, pp. 516, 518, 491, 1882.

[2] Cox, G. H., Copper in southwestern Wisconsin: Min. and Sci. Press, vol. 99, p. 592, 1909.



A. MICROGRAPH OF JASPEROID.

An aggregate of fine-grained allotriomorphic quartz, with sphalerite (shaded) and dolomite that includes minute crystals of quartz. Enlarged 53 diameters,



B. MICROGRAPH OF LIMESTONE BEGINNING TO ALTER TO JASPEROID.

Small quartz crystals are scattered through the limestone.

by Jenney and secondary chert by Winslow, Buckley, and others. Barite is also commonly associated with the ores in central Missouri and in the shallow mines of southeastern Missouri. Jasperoid is the invariable accompaniment of the ores in the sheet ground, and in much of the open ground as well. Dolomite ("spar") is the gangue mineral in much of the open ground above the sheet ground, and is the invariable accompaniment of ore in the rocks of Kinderhook age below the sheet ground. Dolomite occurs also with the jasperoid in the ores in the blanket breccia ground of the Quapaw district, in Oklahoma, as has been previously pointed out by the writer.[1] Where dolomite and jasperoid form the gangue of the ores in the open ground, they are likely to be segregated by regions; that is, the gangue in a mine or closely related group of mines will be almost exclusively either jasperoid or dolomite. For example, the mining area southeast of Joplin is spar ground, whereas that south and west of Joplin is very generally jasperoid ground.

Though the dolomite and jasperoid seem thus to characterize different horizons or different areas, it is nevertheless true that their relation to each other and to the sulphide ores are in places so intimate that they were evidently deposited simultaneously.

OCCURRENCE AND FORMATION OF JASPEROID.

Jasperoid, as has been said, is a dark, fine-grained siliceous rock resembling chert. It forms the matrix of the chert breccia in many of the confused-ground mines and is intercalated with the chert in the sheet ground. It consists of a fine-grained aggregate of quartz crystals and generally contains disseminated grains of sphalerite, galena, or dolomite, or all of them. These grains may be arranged in parallel lines, giving a banded appearance to the rock, as shown in Plate VI, *A* (p. 172). In the interstices between the grains there is considerable bituminous matter, and variations in the amount of the material in places give rise to a finer banding of the jasperoid. The appearance of jasperoid in thin section is shown in Plate VIII, *A* and *B*, illustrations presented by Smith.[2]

The banding of the jasperoid, which closely resembles that of sedimentary rocks, its occurrence in forms resembling mud pockets, its gradation at places into selvage and mud, and its occurrence as the matrix of breccias, as well as other features of it, have led to the general conclusion that it is a silicified mud. Smith made a careful microscopic study of jasperoid, however, and came to the belief that it is almost invariably the result of metasomatic siliceous replacement of limestone. He says:

> It occurs locally in lenticular forms such as characterize the occurrence of limestone in chert, and the manner of its occurrence in sheet ground suggests the replacement of

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[1] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, p. 207, 1908.

[2] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 14, 1907.

sheets and lenses of limestone. More definite evidence is found in the fact that all stages in the process of change from unaltered limestone to jasperoid have been observed, both megascopically and microscopically. Corroborative facts are the occurrence here and there of fossils, particularly crinoid stems, in typical jasperoid, as well as the presence of stylolites in a somewhat calcareous jasperoid at the Jack Johnson mine near Chitwood.

The general process of replacement, as shown by the microscope, is as follows: First a few scattered crystals of quartz appear in the limestone; this stage is seen in Plate VIII, *A*. With increase in the proportion of quartz the limestone decreases till in the later stages the rock consists chiefly of a granular aggregate of quartz with scattered, ragged grains of calcite, mere remnants of the former limestone. Finally even these disappear. Some calcite remnants are often found, even in the occurrences of jasperoid which most resemble mud pockets, and many of the lighter colored of the narrower bands of the banded jasperoid, as already noted, contain residual calcite grains. The quartz in replacing the limestone does not assume the fossil forms shown by the unreplaced calcite, and these forms therefore persist only as long as the calcite remains.

It seems probable, from their mutual relationship, as well as from the fact that sphalerite is found in the limestone with the first appearance of the quartz, but has not been noted in limestone wholly free from quartz, that the sphalerite and quartz have developed simultaneously. That dolomite also has developed at approximately the same time as the quartz seems probable from their microscopic characters as well as their general relations.

This explanation of the origin of jasperoid accounts for the scarcity of limestone in the ore deposits. In the sheet ground limestone is rarely found, jasperoid occupying those positions in which limestone would normally be looked for. In the breccia deposits limestone blocks are sometimes found, but the chert breccia of many mines appears to be wholly free from limestone, although dolomite and chert may border it on one side and limestone with chert on the other. While the relative proportion of chert and limestone in the Boone formation varies both vertically and horizontally, and while the ore breccias occur in the more cherty parts of the formation, nevertheless a considerable amount of limestone would naturally be expected with the breccias in most cases. The replacement of limestone by jasperoid would not only account for the apparent absence of much or most of the limestone to be expected in the chert breccias, especially in those mines which are practically free from dolomite, as the Oronogo mines and those in the hard sheet ground, but would also explain the fractured beds of chert sometimes seen suspended in a matrix of jasperoid.

Under this view selvage is generally a weathered and semidecomposed jasperoid, and much of the black mud is simply the final stage in the weathering and decomposition of the jasperoid.

SILICEOUS REPLACEMENT OF LIMESTONE.

T. Sterry Hunt[1] summarizes in the following words the results of the experimental work of A. H. Church[2] on siliceous replacement:

> He prepared a solution of silica in water by dialysis, according to Graham's method, and found that when this solution, containing about one two-hundredths of silica and impregnated with a little carbonic acid, was filtered through fragments of coral, a large portion of carbonate of lime was dissolved, and the whole of the silica [was]

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[1] Canadian Naturalist, 2d ser., vol. 1, p. 49, 1864.

[2] On the composition, structure, and formation of beekite: London, Edinburgh, and Dublin Philos. Mag. and Jour. Sci., 4th ser., vol. 23, p. 101, 1862; On silica, Chem. News, vol. 5, p. 95, 1862.

> removed [from the solution]. Similar results, though to a less extent, were obtained with shells. In another experiment a fragment of a recent coral was fitted into the neck of a funnel, and a solution prepared as above, with a little carbonic acid and containing one one-hundredth of silica, was allowed to drop on the coral, and after slowly filtering through was found, as in the previous experiment, to have abandoned the whole of its silica, while the coral had lost nearly all its lime, although retaining its structure in a great measure. It was, however, covered with a thick film of gelatinous silica. Mr. Church further observed that the addition of small portions of the solid carbonate of lime, barytes, or strontia to a strong solution of pure silica caused it to gelatinize immediately; and according to Graham solutions of these carbonates have the same effect.

The maximum strength of a solution which did not deposit a portion on standing was that containing six-tenths of 1 per cent of silica; a stronger solution invariably gelatinized after a time.

RÔLE OF COLLOIDAL SILICA IN THE FORMATION OF JASPEROID.

Bain[1] has suggested that the silica of the jasperoid was deposited in a colloidal condition. The facts which led him to this conclusion were: (1) Perfect crystal outline of blende that is completely embedded in the jasperoid; (2) no indication that the blende was deposited in a cavity; and (3) no concentric laminations around the crystals, such as usually occur when a crystal grows in soft sediments.

Kahlenberg and Lincoln[2] have shown that silica is completely hydrolyzed long before the stage of dilution prevailing in natural waters is reached, hence the silica in natural waters must always occur as a hydrolyzed colloid. In Church's experiments, outlined above, it was found that the addition of a small portion of solid calcium carbonate or of a solution of calcium carbonate to a strong solution of silica caused it to gelatinize immediately. When a recent coral was treated with a solution of silica charged with carbon dioxide, it was found that the calcium carbonate had been replaced by silica. The replaced coral was covered with a thick film of gelatinous silica and was very soft. Bain cites Le Conte[3] as speaking of the silica at Sulphur Bank as so recent as to be still gelatinous, and notes Weed's[4] description of the sinter deposits of the Yellowstone National Park as showing that the silica in hot springs, at least, goes through a colloidal state, taking eventually an amorphous or opaline form. Levings[5] describes several occurrences of gelatinous silica as follows:

> About four years ago, when the writer was connected with the Great Australia mine, Cloncurry, Queensland, a drive was beat out under the siliceous copper outcrop.

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[1] Bain, H. F., Van Hise, C. R., and Adams, G. I., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 106-107, 1901.

[2] Kahlenberg, Louis, and Lincoln, A. T., Solutions of silicates of the alkalies: Jour. Phys. Chem., vol. 2, pp. 77-90, 1898.

[3] Le Conte, Joseph, On the genesis of metalliferous veins: Am. Jour. Sci., 3d ser., vol. 26, p. 9, 1883.

[4] Weed, W. H., Formation of travertine and siliceous sinter by the vegetation of hot springs: U. S. Geol. Survey Ninth Ann. Rept., pp. 613-676, 1889.

[5] Levings, J. H., Discussion of an article on "Gels in relation to ore deposition": Inst. Min. and Met. Trans., vol. 21, pp. 478-479, 1912.

> Water was continuously flowing through this ore body, which acted as a drainage conduit for the surrounding country. Numerous vugs were cut into, and silica in all stages of gelatinization was found, varying from a viscous fluid to veins which could be cut with a knife, like cheese. The writer dehydrated many samples; some were practically pure silica, some contained carbonate of lime and carbonates of copper. In other samples taken from solidified portions a complete gradation from silica to calcite could be followed. Apparently silica and calcite can be precipitated from the same solution in any proportions. It may be mentioned that the lode occurs in diorite.
>
> Some years previously, in Tasmania, some jellylike substance was brought for the writer to determine. It had been obtained from a vug in a siliceous copper lode, and contained some free slender quartz crystals about 2 inches long, both ends of which terminated in prisms. Some similar but better proportioned crystals about one-half inch long were also present. On examination the substance was found to be silica in a gelatinous state. The lode occurred in old sedimentary rocks.

In this connection there should be noted the description (pp. 186–187) of the sediment from White Sulphur Spring. In this spring quartz, calcite, and pyrite are depositing simultaneously.

Hatschek and Simon,[1] applying the principle of phenomena like Liesegang's rings to ore deposition, made a number of experiments with a gold salt dissolved in colloidal silicic acid in a test tube, pouring a reducing solution on top. Bands of precipitated metallic gold were formed in the silicic acid, parallel to its upper surface, which were analogous to the rings of Liesegang. The authors argue that these experiments indicate that auriferous quartz veins in which the gold occurs in bands are due to this sort of diffusion rather than to crustification. They say:[2]

> When piercing the Simplon tunnel a vein of silicic acid in the gelatinous condition was discovered, and it does not therefore seem too daring to assume a gelatinous state as the transition between the original liquid and the ultimate solid form of a quartz vein. The solution which contained the silicic acid may also have contained the gold salt, and when this solution set to a gel this salt would be distributed uniformly throughout. It is, however, possible also that the silicic acid set to a gel first, after which the gold diffused into it. The reduction or precipitation of the metal was a subsequent process, and the reducing agent, as far as some alluvial deposits are concerned, most probably was a gas. * * *
>
> Quartz veins with banded structure find a ready explanation with the formation of the strata mentioned in experiment No. 6. If we again assume a vein of gelatinous silicic acid with uniform gold contents, and we assume surface waters containing the reducing agent to follow the quartz vein from the surface downward through the salbands, we obtain ultimately a vein with bands of rich quartz lying parallel to the vein walls at the outcrop, gradually decreasing in richness as depth is attained, and simultaneously losing the banded appearance.

Brief reference has been made to the banded character of the jasperoid. A view of a specimen of jasperoid exhibiting typical fine banding is shown in Plate VI, *A* (p. 172). Smith[1] describes it somewhat in detail as follows:

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[1] Hatschek, E., and Simon, A. L., Gels in relation to ore deposition: Inst. Min. and Met. Trans., vol. 21, pp. 451–459, 1912.

[2] Idem, pp. 456–457.

> Here and there the jasperoid is marked by bands of greater or less width. The coarser banding is due to variations in the amount of contained sphalerite or dolomite. The finer banding is in lighter and darker shades of gray, and, as shown by the microscope, is due to variations in the amount of interstitial bituminous matter, depending on differences in texture, or to variations in mineral composition, such as the occurrence of calcite in some of the bands. Some of these finer bandings are curved, but most of them are horizontal or nearly so and parallel to the broader bands. Many of them are near and parallel to the upper surface and some extend only a part of the way across an exposure of the rock.

The resemblance of the banding of jasperoid to the banding obtained in the experimental work of Hatschek and Simon and others is marked. It seems not unreasonable to suppose that in certain favorably situated areas gases may have collected above the colloidal jasperoid and effected the rythmic precipitation of the metals and the dolomite, while the bitumen collected in the interband areas. Such a colloid would not offer strong hindrance to the diffusion of the ore-bearing solutions or to the expansion of the growing ore crystals. Again, such a colloidal mass would be effective as a support for the smaller chert fragments, the present position of which indicates that they floated in the nascent jasperoid matrix. Even if a portion (perhaps the major portion) of the jasperoid originated through the replacement of limestone, as determined by W. S. T. Smith, the replacing silica may for a time have been in a colloidal state.

OCCURRENCE AND FORMATION OF DOLOMITE.

Dolomite occurs in three forms in the Joplin region. A fine-grained buff variety evidently resulted from the dolomitization of the limestone in place without alteration of the bedding, for such beds of dolomite may at places be followed directly into unaltered beds of limestone. Though nowhere associated with areas of mineralization this form of dolomite is usually found where the rocks have been considerably disturbed by solution. This kind of dolomite is similar in texture to all the widespread formations of dolomitic limestone. A second variety of dolomite, usually called "gray spar," occurs in large bodies of massive coarse granular texture, which lie adjacent to the ore in many of the ore bodies of the area. The crystals of dolomite in this variety of the rock are many times larger than those in the variety first mentioned, and show the curved faces characteristic of the mineral. The third variety of dolomite is known as "pink spar" and occurs in veins in both the foregoing varieties, or forms the lining of cavities or pockets in them. This variety and calcite line cavities in the ore bodies in many places where the massive varieties of dolomite do not occur, as, for instance, in chert ground. The crystals in pink spar are larger than those in gray spar, are pink in color, and are typically saddle shaped with curved faces.

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 13, fig. 21, 1907.

The following petrographic description of the dolomite of the region and discussion of its origin is given by Smith:[1]

> The dolomite grains have in few or no cases the medium or dark gray color which characterizes the rock as a whole, being usually pale gray with a pink tinge, which locally affects the rock mass. The common dark color of the rock is due to interstitial matter, ordinarily seen megascopically as numerous small dark-gray or brown to blackish specks. The amount of these impurities is variable, but all the dolomite contains them to a greater or less extent. The dolomite has as a rule a rather tough surface of fracture, on which the rhombohedral forms of many of the grains may often be made out.
>
> Microscopically the texture of the dolomite approaches panidiomorphic granular. The angular spaces between the grains are most commonly filled with jasperoid, which contains in places a small proportion of dolomite and is usually of a brownish color from bituminous impregnation; but in many specimens bituminous matter forms the predominant filling of the intergranular spaces, in which case they are generally dense or opaque. These bituminous areas form the dark specks seen in the hand specimen.
>
> Jasperoid was found in the majority of the massive dolomites examined. It occurs intermixed with the dolomite in all proportions, though as a rule the amount is small. Analyses indicate approximately, by the percentage of silica, the proportions of jasperoid commonly present in these dolomites. As already noted, jasperoid and dolomite are sometimes found grading into each other.
>
> That the massive dolomite has been formed by the dolomitization of limestone is shown by the general limitation of its occurrence to the ore deposits, by the inclusion in it of beds and lenses of chert, and by the local occurrence of limestone in the process of passing over into dolomite. In this process the fossils are as a rule completely obliterated.

DOLOMITE AND JASPEROID IN THE ASPEN DISTRICT, COLO.

The gangue minerals associated with the ore deposits of the Aspen district of Colorado are very similar to those that accompany the ore deposits of the Joplin district. There, as in the Joplin district, the ores are associated with jasperoid and dolomite. Barite is plentiful at Aspen. It is not plentiful in the Joplin district, but it is plentiful in central and southeastern Missouri. Spurr[2] says:

> This local dolomization almost invariably accompanies the ore. Even when the latter is in blue limestone there is usually a sort of envelope of dolomite around it, which in turn is surrounded by the limestone. In rare cases, when the ore is directly inclosed in blue limestone without such an envelope, its analysis shows the presence of magnesia, while the limestone is almost entirely pure.
>
> The microscope affords means to trace the alteration of the blue foraminiferal limestone into dolomite in its various stages. In this process the coarse calcite be-

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 14, 1907.

[2] Spurr, J. E., Geology of the Aspen mining district, Colo.: U. S. Geol. Survey Mon. 31, pp. 210-211, 1898.

> comes broken up into smaller crystals, which assume the rhombohedral form and the yellowish tinge distinctive of dolomite. The characteristic structure of the blue limestone persists for a time during this alteration, but becomes fainter as the crystallization proceeds. The coarsely crystalline calcite and the cryptocrystalline variety which form the two distinct phases of the blue limestone both become finely crystalline dolomite, but the texture of the two varieties continues different for some time. The dolomite often incloses small grains of pyrite or is stained by disseminated limonite.

Spurr finds that the local dolomitization, associated with water-courses, is not due to the surface water of the present time for, describing certain springs and waters inflowing along faults, he says:[1]

> These waters, which evidently come mainly from the surface, do not appear to exercise any dolomizing influence on the limestone which they traverse, and the phenomena of dolomization, silicification, and ore deposition along the faults show that the waters which produced them were in some way more potent than the cold waters which now circulate underground.

At Glenwood Springs, Colo., 40 miles from Aspen, Spurr found that the water of the Yampa Spring (No. 31 in the synoptical table and table of analyses) was accomplishing a dolomitic replacement of the limestone on the side walls of its channels. This water contains free carbon dioxide and hydrogen sulphide in notable quantities. Spurr gives analyses of the wall rock taken from different places to show that there is a progressive increase in the magnesia and silica content of the rock in proportion as the water has had access to it. His description of the progressive alteration of limestone to jasperoid is very similar to the description by W. S. T. Smith of the similar replacement in the Joplin district (pp. 179–180). Spurr[2] concludes that the dolomitization and the silicification were contemporaneous, as follows:

> From the association of jasperoid with dolomite belonging to the second period, as well as from the evidence which microscopic study affords, it is clear that the quartz was deposited at the same time and under the same conditions as the magnesia. In the case of the dolomite the conclusion has been arrived at that the change from limestone has been brought about by ascending magnesia-bearing waters, and it has been shown that such a change is now going on at Glenwood Springs. The comparative analyses which were cited to prove this phenomenon at Glenwood Springs also show an accompanying silicification, which is actually being brought about by the ascending hot waters.

SPRING DEPOSITS AT SULPHUR SPRINGS, ARK.

In the northwest corner of Arkansas, at the village of Sulphur Springs, there is a group of springs, two of which, known respectively as White Sulphur Spring and Black Sulphur Spring, have lately been described by the writer.[3] The springs emerge in the valley of Butler Creek, the rock underlying which belongs to the "Yellville formation," of Ordovician age. The Chattanooga shale outcrops in the hills at an altitude of about 50 feet above the floor of the valley. The springs are walled up and cemented, their basins being about 2 feet in diameter and 6 feet deep. The temperature of the water is that of the basin, and is the mean annual temperature of the region for that depth. Both springs contain noticeable quantities of hydrogen sulphide gas and deposit a sediment in the bottom of the basin. The sediment from the White Sulphur Spring is almost black. The water from this spring is No. 35 in the synoptical table (p. 150). Analyses of these sediments, given in the table of analyses of reservoir sediments (p. 164), show the presence of lead, zinc, copper, and iron in each. Megascopic examination of the sediments shows the presence of a considerable quantity of crystallized pyrite in each. In the hope that the microscope might reveal some crystals of sphalerite or galena, the sediments were submitted for closer examination to H. E. Merwin, of the Geophysical Laboratory of the Carnegie Institution. The results of this examination, though disappointing in not yielding crystallized sphalerite or galena, are nevertheless valuable and interesting and are given herewith.[1]

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[1] Spurr, J. E., op. cit., p. 212.

[2] Idem, pp. 220–221.

[3] Siebenthal, C. E., Spring deposits at Sulphur Springs, Ark., with microscopic examination by H. E. Merwin: Econ. Geology, vol. 9, pp. 758–767, 1914.

MICROSCOPIC EXAMINATION OF DEPOSITS OF SULPHUR SPRINGS.

By H. E. Merwin.

Black Sulphur Spring.—The noteworthy constituents of the sediments are quartz grains and quartz crystals, pyrite, and impure calcite concretions.

Many of the irregular grains of quartz and also those that still retain crystal outlines have been so much corroded that their surfaces are spongy.

The calcareous concretions are not numerous and are small (diameter about 0.5 millimeter). They have radial structure but irregular surfaces. The refractive index of crushed fragments is considerably higher than that of pure calcite, but the concretions effervesce freely in cold dilute acid and the resulting solution reacts for iron, evidently showing that the concretions are not dolomitic. The maximum refractive index, 1.69 – 1.71, is too high for aragonite.

The pyrite occurs in nodular aggregates, the largest about 3 millimeters in diameter, and in single crystals as large as 0.4 millimeter in diameter. The cube and octahedron are the only forms recognized. The cube faces show no striations and are much less bright than the octahedron faces. By growing into the spongy surfaces of quartz grains the pyrite becomes firmly attached and joins the grains into groups.

Many small sharp-angled, bright-faced quartz crystals, 0.5 millimeter in diameter, were attached to etched quartz grains in such a way as to indicate that deposition of quartz takes place in parts of the spring, probably at a distance from the source of supply.

White Sulphur Spring.—Pyrite and calcite are the only minerals that appear to be depositing in this spring. The pyrite is in nodules and single crystals, as in the other spring.

Distinct calcite crystals 0.2 millimeter long were seen on a piece of iron wire taken from the spring. Smaller crystals form an oozy deposit, and other small crystals are aggregated into heavy grains. All these crystals have the optical properties of nearly pure calcite.

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[1] Siebenthal, C. E., op. cit., pp. 765–766.

The grains of quartz, pyrite, and calcite are etched and pitted, but to a very much less degree than in the Black Sulphur Spring. Many of these grains are double pyramids with angles only slightly rounded. Their origin is not known.

The cited analyses of the waters of White Sulphur Spring and of Black Sulphur Spring and their sediments show that they have a high content of chlorides and alkali metals, similar to that of the deep-well waters, and that, like many of those waters, upon standing they deposit a dark sediment which contains the metals as sulphides. The sediments differ from most of those deposited by deep-well waters, however, in containing crystallized sulphide of iron, calcite, and quartz. It was to be expected that the sediments might show dolomite as well as calcite, for the waters contain relatively large proportions of magnesium, but the microscope revealed no trace of crystallized dolomite, and the analyses of the sediments show that the magnesium is deposited in relatively small quantities. Nevertheless, it appears to the writer that these waters, which come from the same geologic horizon as the deep waters of the Joplin region and are similar to them and to the Miami mine waters in quality and that deposit, as those waters do, calcite, quartz, metallic sulphides, and crystallized pyrite, were undoubtedly capable not only of depositing the ores of the Joplin region but also the gangue minerals and rocks, calcite, secondary limestone, dolomite, and jasperoid.

COMPARISON OF ACTION OF SURFACE AND ARTESIAN WATERS IN RELATION TO THE FORMATION OF JASPEROID AND DOLOMITE.

If, as Smith[1] has shown, the jasperoid and dolomite that accompany the ores were formed by replacement of limestone, the replacement was doubtless effected by the ore solutions. If it can be shown that ascending solutions were better constituted to accomplish this replacement than laterally moving solutions or solutions descending from the Pennsylvanian above, we may cite the occurrence of the jasperoid and dolomite with the ores as evidence of the artesian theory of the origin of the ores.

Winslow[2] points out that a tongue of Mississippian rocks extends from the Joplin region eastward toward the center of the Ozark region and infers that this was probably a trough during the erosion interval just antedating the Pennsylvanian deposition. The erosion of the Cambrian and Ordovician dolomites higher on the dome would supply magnesium to the waters flowing down this trough and result in the local dolomitization of the Mississippian limestone.

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 14, 1907. See quotations on pp. 179–180 and 184 of this report.

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, p. 485, 1894.

Buckley and Buehler[1] believe that the shales and thin beds of limestone of the Pennsylvanian series are the source of the magnesium required to form the dolomite, the metal being taken into solution from those rocks as they were weathered and eroded, and the solution being carried down into the Mississippian rock, producing local dolomitization.

Bain[2] holds that the ore metals and the magnesium were derived from the dolomitic limestones of the Cambrian and Ordovician and brought into their present situation by the water of the artesian circulation, which also carried the silica that locally replaced the limestone by jasperoid. The writer also holds this view.

The following tables show the silica and magnesium content of the waters of springs in the Pennsylvanian shales—waters, according to the hypothesis of Buckley and Buehler, representing descending solutions; of springs in the Mississippian limestones representing the laterally moving solutions, considered by Schmidt and others; and of waters of deep wells drawing their supply from the Cambrian and Ordovician rocks, representing the ascending artesian solutions considered by Bain, Smith, and the writer. The analyses given in the first table have been compiled from Schweitzer;[3] the others are compiled from tables of analyses given on pages 124–140.

Silica, calcium, and magnesium content of waters of springs supplied from Pennsylvanian rocks of Missouri.

[Parts per million.]

	Silica (SiO_2).	Calcium (Ca).	Magnesium (Mg).	Reacting weight of Ca (rCa).	Reacting weight of Mg (rMg).	Ratio of rMg to rCa.
Clay County:						
Sulpho-saline Spring	10.1	238.96	98.7	11.9	8.1	1:0.68
Rogers Spring	43.1	73.6	10.5	3.7	.9	1:0.24
Siloam Springs	26.1	98.7	7.2	4.9	.6	1:0.12
Regent Spring	19.1	121.9	13.6	6.1	1.1	1:0.18
Reeds Spring	20.0	65.2	6.9	3.3	.6	1:0.17
Henry County:						
Sand Creek Spring	18.0	45.9	16.3	2.3	1.3	1:0.58
Windsor Spring	12.0	3.7	2.5	.19	.21	1:1.12
Ford Spring	8.8	436.9	70.3	21.8	5.8	1:0.26
Jackson County:						
Cusenbury Spring	18.0	87.2	8.8	4.4	.7	1:0.17
Lithia Spring	26.0	100.9	16.9	5.0	1.4	1:0.28
Greenwood Spring	57.0	10.6	1.3	.5	.1	1:0.21
Johnson County:						
Post Oak Sulphur Spring	9.9	49.0	21.7	2.4	1.8	1:0.73
Pertle	28.5	66.3	19.1	3.3	1.6	1:0.48
Reeds Spring	16.8	28.7	4.4	1.4	.4	1:0.25
Colburn Spring	26.8	141.8	30.1	7.1	2.5	1:0.35
Average	22.7	104.6	21.9	5.2	1.8	1:0.39

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[1] Buckley, E. R., and Buehler, H. A., The geology of the Granby area: Missouri Bur. Geology and Mines, vol. 4, p. 21, 1906.

[2] Bain, H. F., Van Hise, C. R., and Adams, G. I., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 209–211, 1901.

[3] Schweitzer, Paul, A report on the mineral waters of Missouri: Missouri Geol. Survey, vol. 3, 1892.

Silica, calcium, and magnesium content of waters of springs supplied from Mississippian rocks in the Joplin region.

[Parts per million.]

	No. in tables of analyses.	Silica (SiO_2).	Calcium (Ca).	Magnesium (Mg).	Reacting weight of Ca (rCa).	Reacting weight of Mg (rMg).	Ratio of rMg to rCa.
Cox Spring, Mo	87	15.0	42.6	2.5	2.1	0.2	1:0.10
B. & C. mine water, Mo	101	14.9	127.1	8.7	6.3	.7	1:0.11
Chico Spring, Kans	102	17.5	45.8	6.8	2.3	.6	1:0.24
Cave Spring, Kans	109	22.7	19.8	1.6	1.0	.1	1:0.13
Lakeside Spring, Mo	110	9.7	107.4	6.5	5.4	.5	1:0.10
Average	......	16.0	68.5	5.2	3.4	.4	1:0.14

Silica, calcium, and magnesium content of deep-well waters in Ozark region.

[Parts per million.]

Name or owner of well.	No. in tables of analyses.	Silica (SiO_2).	Calcium (Ca).	Magnesium (Mg).	Reacting weight of Ca (rCa).	Reacting weight of Mg (rMg).	Ratio of rMg to rCa.
Missouri:							
Nevada	27	14.0	80.1	32.6	4.0	2.7	1:0.67
Clinton No. 2	32	4.0	80.4	36.6	4.0	3.0	1:0.75
Silver (to 1,100 feet)	38	8.8	115.1	56.6	5.7	4.7	1:0.81
Britts	40	14.0	105.8	44.4	5.3	3.6	1:0.69
Clinton No. 1	42	11.7	116.7	50.1	5.8	4.2	1:0.72
Brunswick	51	5.0	739.7	329.2	36.9	27.1	1:0.73
Silver (below 1,100 feet)	55	9.0	196.9	234.5	9.8	19.3	1:1.96
Belcher	56	2.4	495.0	180.0	24.7	14.8	1:0.60
Cornfield	64	10.8	53.3	7.2	2.7	6	1:0.22
Missouri Lead & Zinc Co. (depth 1,387 feet)	68	10.0	37.0	17.1	1.8	1.4	1:0.76
Oronogo	76	8.4	39.3	14.8	2.0	1.2	1:0.62
Missouri Lead & Zinc Co. (depth 940 feet)	82	14.2	44.0	21.7	2.2	1.8	1:0.81
Freeman Foundry	84	7.2	52.8	16.3	2.6	1.3	1:0.51
Fulton	86	15.1	68.6	38.2	3.4	3.2	1:0.93
Harrington	88	9.1	35.0	15.9	1.7	1.3	1:0.75
Providence	89	16.8	37.7	17.3	2.0	1.4	1:0.72
Alba	91	12.3	79.0	6.2	3.9	.5	1:0.13
Redell	92	47.7	40.3	12.8	2.0	1.1	1:0.52
Ash Grove	95	9.8	39.2	19.0	2.0	1.6	1:0.80
Webb City	96	10.1	37.9	16.1	1.9	1.3	1:0.70
Freeman Foundry	98	35.0	52.0	5.0	2.6	.4	1:0.16
Kansas:							
Columbus	5	6.7	43.3	22.1	2.2	1.8	1:0.84
Cherokee	13	8.9	62.2	31.3	3.1	2.6	1:0.83
Fort Scott	33	16.3	69.5	35.4	3.5	2.9	1:0.84
Pittsburg waterworks	90	10.7	68.4	29.3	3.4	2.4	1:0.70
Pittsburg (No. 3)	103	9.2	65.6	31.2	3.3	2.6	1:0.78
Oklahoma:							
Vinita	15	10.3	21.3	8.4	1.1	.7	1:0.66
Nowata	20	42.2	5,604.1	1,045.3	279.6	87.6	1:0.31
Afton	23	13.2	31.2	12.3	1.6	1.1	1:0.68
Whitaker Park	25	9.6	183.5	65.1	9.2	5.3	1:0.58
Miami	34	9.5	32.2	14.9	1.6	1.2	1:0.76
Brown	45	....	1,486.0	472.7	74.1	39.2	1:0.53
Radium	46	....	1,480.0	487.9	80.6	40.5	1:0.50
Fairland	77	....	36.3	18.7	1.8	1.6	1:0.86
Average	......	13.29	344.98	101.36	17.414	8.41	1:0.69

Silica, calcium, and magnesium content of spring and well waters in the Ozark region.

[Parts per million.]

	Silica (SiO_2).	Calcium (Ca).	Magnesium (Mg).	Reacting weight of Ca (rCa).	Reacting weight of Mg (rMg).	Ratio of rMg to rCa.
Average of 15 springs supplied from Pennsylvanian rocks	22.7	104.6	21.9	5.2	1.8	1:0.39
Average of 5 springs supplied from Mississippian rocks	16.0	68.5	5.2	3.4	.4	1:0.14
Average of 34 wells drawing water from Cambrian and Ordovician rocks	13.3	345.0	101.4	17.4	8.4	1:0.69
White Sulphur Spring, Benton County, Ark., supplied from Ordovician rocks	7.4	35.9	16.3	1.8	1.3	1:0.75
Yampa Spring, Colo	33.7	568.5	95.0	28.4	7.8	1:0.27
Ocean (Dittmar's analysis)	2.5	420.0	1,316.0	21.0	108.2	1:5.15

The table last presented shows that the average spring water in Pennsylvanian rocks is well supplied with silica and contains a fair proportion of magnesium to calcium. The waters of the springs in the Mississippian rocks, on the contrary, contain much less silica and only about one-third as much magnesium in proportion to the calcium. The waters from the deep wells, though containing still less silica, carry nearly twice as much magnesium in proportion to calcium as the waters from the Pennsylvanian rocks and about five times as much as the waters from the Mississippian rocks. The consideration of these facts would naturally lead to the conclusion that the waters from the Pennsylvanian rocks would be the most effective in silicification and that the deep-well artesian waters would be the most effective in dolomitization.

The table also shows the silica, lime, and magnesia content of water from White Sulphur Spring, at Sulphur Springs, Ark., and from Yampa Spring, at Glenwood Springs, Colo. Classified by geochemical character both these spring waters, as shown in the synoptical table (p. 150), fall among the deep-well waters of the Joplin region and resemble the water of the ocean, according to Dittmar's analysis (No. 52 in the synoptical table), although ocean water contains a much higher proportion of magnesium to calcium than the well waters. The average well water contains about seven-tenths as much total reacting weight of magnesium as of calcium, whereas the total reacting weight of magnesium in ocean water is more than five times as great as that of calcium. It is very generally believed that widely extended beds of fine-grained dolomite the world over have been formed on the bottom of the sea by the reaction of unconsolidated calcareous deposits with the magnesium salts held in solution in sea water.

In the deep artesian waters of the district, then, we have: (*a*) Waters that, in their content of carbon dioxide and silica, resemble the experimental solution with which Church obtained a siliceous replacement of limestone; (*b*) waters that closely resemble the water of Yampa Spring, which, as Spurr has shown, dolomitizes and silicifies the wall rock of its channel; (*c*) waters that, except in degree of concentration and relative proportion of magnesium to calcium, are closely related to sea water; and (*d*) waters that are identical with the waters of Sulphur Springs, Ark., which are depositing crystallized quartz, calcite, and pyrite, as well as uncrystallized sulphides of lead, zinc, and copper.

Waters of this kind, carrying a relatively high content of magnesium, on rising to the surface under artesian pressure through nonmagnesian limestones exchange magnesium for calcium through mass action. The carbon dioxide in the water, which is in part combined with magnesium to form magnesium bicarbonate and in part combined with the heavy metals to form bicarbonates will enter into a new combination with the calcium of the limestone, taking it into solution and throwing down magnesium and the metals. It may reasonably be inferred that such water must deposit also silica, and this inference is confirmed by Spurr's observations of the action of the water of Yampa Spring and by the results of Merwin's examination of sediments from Sulphur Springs, Ark. As the supply of the solutions is constantly renewed the dolomitization and silicification will progress until the final result is dolomite and jasperoid.

ABSENCE OF DOLOMITE AND JASPEROID IN MISSISSIPPIAN ROCKS BENEATH THE PENNSYLVANIAN IN OTHER REGIONS.

The writer is familiar with the unconformable contact of the Pennsylvanian and Mississippian rocks in Indiana and has not there seen either jasperoid or dolomite in the underlying limestones of the Mississippian, such as should have occurred if dolomitization and the formation of jasperoid were produced by surface waters deriving their magnesium and silica from the Pennsylvanian shales. As Bain[1] has pointed out, the reports of the geological surveys of Illinois and Iowa appear to record no observation of the presence of dolomite or jasperoid in the Mississippian rocks that immediately underlie the Pennsylvanian in those States. Neither has the writer observed dolomite or jasperoid in limestones of Mississippian age in contact with the Pennsylvanian rocks at points remote from ore deposits in that part of Arkansas or Oklahoma with which he is familiar. He has traversed the outcrop of Fort Scott limestone for nearly a hundred miles and has seen no jasperoid or dolomite in that limestone, yet it is intercalated between two shale formations of the Pennsylvanian system and is in a position where it was likely to be affected by waters passing through the Pennsylvanian shales. Buckley[1] notes the occurrence in southeastern Missouri of fine marble beds in the series of shales and limestones which has been called the Davis formation and remarks that a large number of beds of limestone occur in the formation, though the overlying and underlying formations are essentially dolomites.

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[1] Bain, H. F., Review of special report on lead and zinc by E. Haworth and others: Econ. Geology, vol. 2, p. 190, 1907.

CONCLUSION.

Both the megascopic and the microscopic character of the ore and gangue shows that the ores, the jasperoid, and the dolomite, were deposited from the same solution, for the most part simultaneously and in the main as by replacement of limestone. The experiments of Church (see pp. 180–181) show that in solutions containing silica and carbon dioxide limestone is replaced by silica. The solutions from which the ores, the dolomite and the jasperoid, were deposited must therefore have contained carbon dioxide, silica, calcium, magnesium, the metals of the ores, and hydrogen sulphide or sulphate radicle in order to cause the precipitation of the metals as sulphides. The artesian deep-well waters of the region contain these substances, and they are now depositing the metals as sulphides in reservoir sediments. Sea water, the greatest agent of dolomitization, if classified geochemically, falls near the deep-well waters. The water of the Yampa Spring, which, as Spurr shows, has both silicified and dolomitized the limestone adjacent to its channel, falls near the deep-well waters in the geochemical classification and has similar characteristics. The water from White Sulphur Spring at Sulphur Springs, Ark., also falls near the water of Yampa Spring in the classification. Chemical analysis of sediment from this spring and from the similar Black Sulphur Spring shows they deposit zinc, lead, copper, and iron. Microscopic analyses of the sediments show that the springs are depositing crystallized pyrite, quartz, and calcite. Dolomite and jasperoid have not elsewhere been formed in the limestones below the Pennsylvanian, where the circulation was never artesian. In the Joplin region, as is shown on a later page, dolomite, jasperoid, and ore are not found above the Chattanooga shale where that formation is continuous and efficient as a barrier to ascending solutions.

It may therefore be concluded that the association of dolomite and jasperoid with the ore deposits of the Joplin region is evidence that they were formed by ascending solutions similar to the artesian circulating water now rising in deep wells in the Pennsylvanian area west of the Joplin region.

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[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, vol. 9, p. 43 [1909].

RELATION OF THE JOPLIN ORE DEPOSITS TO THE CHATTANOOGA SHALE.

ORE DEPOSITS AT THE HORIZON OF THE CHATTANOOGA SHALE.

Buckley and Buehler have formulated a critical test for the theory that the Joplin ores were deposited from circulating artesian water. This test involves the relations of the deposits to the Chattanooga shale and, in substance, is that the ascending metal-bearing solutions, coming into contact with the "Devono-Carboniferous" shale, should have their metals precipitated in part by the organic matter of the shale or by the hydrogen sulphide gas originating in the shale, and that deposits of average or greater richness in lead should be formed at or near the horizon of the shale. They say:[1]

> As this circulation starts upward, through the Devono-Carboniferous shales, it will be brought at once into contact with the very abundant organic matter which the third premise above would cause these shales to contain. As already shown, the presence of this organic matter forms reducing conditions and the source of hydrogen sulphide. The latter is probably the main precipitant of organic origin, and in this discussion will be the precipitant referred to.
>
> The instant hydrogen sulphide is introduced into the solutions carrying lead and zinc salts we have the conditions for precipitation. As a result, the sulphide would be deposited soon after leaving these shales, if not actually within them. Considering the solutions as either alkaline or neutral, the hydrogen sulphide would at once precipitate, together, the lead, zinc, and probably the iron as sulphides. If the alkaline sulphides were present in abundance, the iron might remain in solution as described on pages 94 and 95, not being precipitated until coming in contact with acids or other salts coming from surface waters, in which case the iron sulphide would certainly be concentrated at a very high level, probably near the level of the underground water. * * *
>
> Had the upward circulating waters been acid, which would hardly be the case under the conditions cited, the hydrogen sulphide would at once have precipitated the galena, while the zinc and iron would have been carried upward until neutralization had taken place, when they in turn would have been deposited. We would therefore, in the case of an ascending acid solution, have obtained a vertical segregation of the ores, with the galena occurring below the blende and pyrite. Thus, no matter what the original nature of the single ascending solution, there would be formed within or starting directly above the Devono-Carboniferous shales either an intimate mixture of the sulphides of lead, zinc, and iron, showing little or no vertical segregation, or one in which galena has been concentrated largely at the base of the deposits, near the Devono-Carboniferous shales. * * *
>
> We know of no way by which the galena precipitated in the primary deposits in the lower part of the formation could become segregated at upper levels by secondary concentration. Consequently, the galena should occur intimately mixed with sphalerite and pyrite in the primary deposits, under the conditions cited, wherever these primary deposits are found. Furthermore, galena of undoubted primary concentration should occur down to the Devono-Carboniferous shales. * * *
>
> If the ascending circulation carried the metallic salts and the required organic or reducing material were present in the shales, the conditions necessary for deposition

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[1] Buckley, E. R., and Buehler, H. A., The geology of the Granby area: Missouri Bur. Geology and Mines, vol. 4, pp. 107-110, 1906.

were evidently present throughout this part of the formation. If this were the case, it is hard to conceive why uniformly throughout the district the deposits do not occur in this portion of the formation.

The writer has pointed out that the term "Devono-Carboniferous shale" was used by Bain to denote the Devonian Chattanooga shale and the Carboniferous shale of Kinderhook age. Only one of these, the Chattanooga shale, is notably rich in organic matter and can be regarded as a precipitant for the solution. As the Chattanooga shale is not widely distributed in the Joplin region, ore deposits should not occur in that formation "uniformly throughout the district."

Three conditions are necessary in order to subject the artesian theory to this test, namely, (*a*) the Chattanooga shale must be present; (*b*) ore deposits must exist in the upper strata in the area in order to show that conditions will permit solutions to ascend through the shale; (*c*) sufficient deep drilling must have been done to establish the presence or absence of ore at the postulated horizon.

The first condition eliminates all but one of the main producing camps of the Joplin district. Granby is the only important camp underlain by the Chattanooga shale. Fortunately, Granby has also been the scene of systematic drilling that reached to or beyond the Chattanooga shale. The Granby Mining & Smelting Co. has very kindly furnished two charts of deep drilling in that region, dated July, 1907, and March, 1909. The area covered by these charts comprises 160 acres in sec. 31, T. 26 N., R. 30 W., just north of the town of Granby. From these two charts all the sections that represent drill holes which undoubtedly reach the Chattanooga shale have been arranged in linear order on the accompanying chart (Pl. IX). The records of shallow drill holes and holes not reaching the Chattanooga shale have been omitted. The horizon of the Chattanooga shale is that identified by Buckley and Buehler as "Devono-Carboniferous."[1] Inspection of the chart will show a very persistent ore horizon at the level of the Chattanooga shale. The irregularities of level that may be observed are due largely to the fact that the elevation of the surface was not taken into account in charting the records.

An analysis of the charts of this drilling just north of Granby shows that 52 drill holes reached the horizon of the Chattanooga shale. Of these, 34 report "selvage" or "clay," the driller's terms for soft shale, at the horizon of the shale. The shale was probably struck in a number of the other drill holes, but its occurrence in them is not noted on the charts, the narrow space in the columnar sections being taken up in delineating the ores found at that horizon. In several places, however, there is neither ore nor any indication of the shale, from which it must be inferred that the shale is not persistent so near

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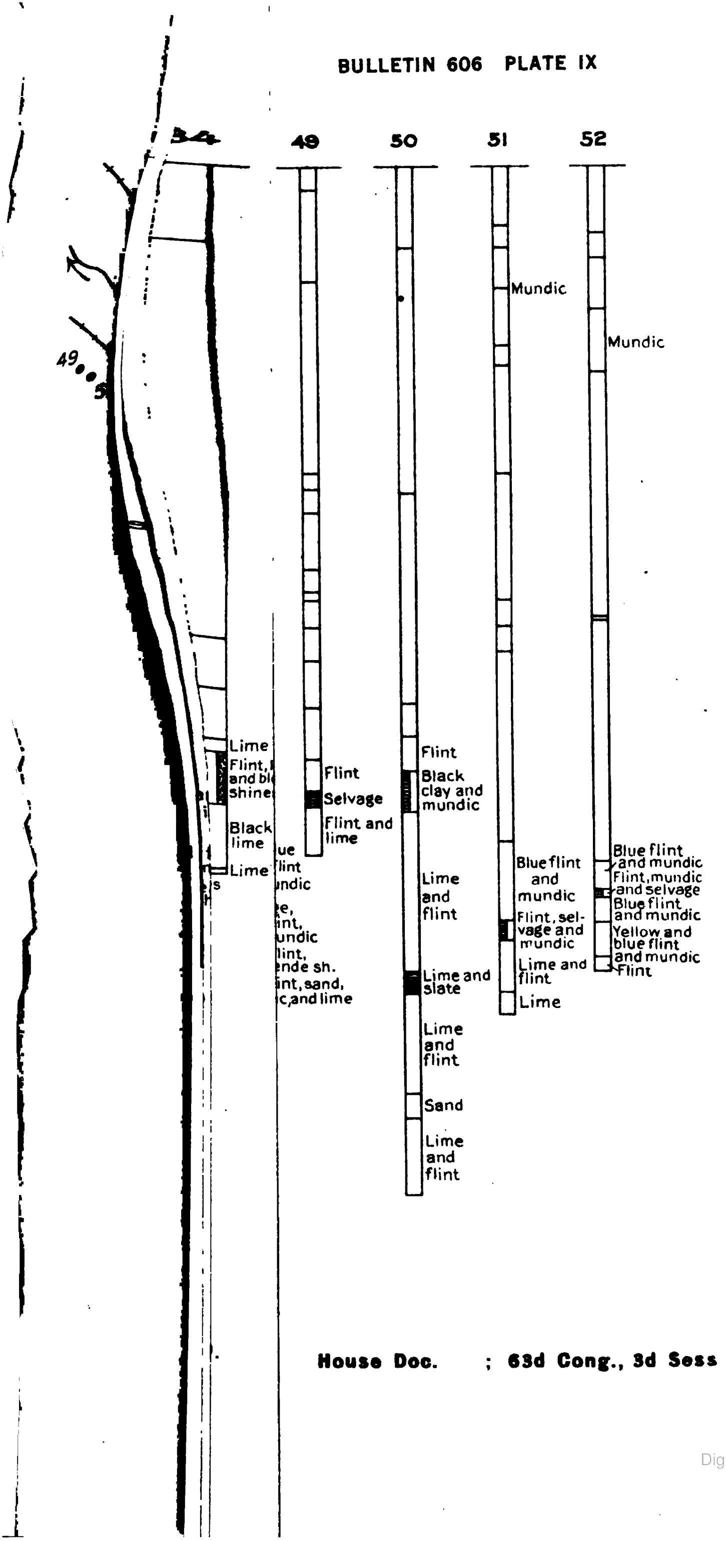
[1] Buckley, E. R., and Buehler, H. A., op. cit., Pl. V, facing p. 29.

BULLETIN 606 PLATE IX



to its northern limit. Of the 52 holes that reach the horizon of the shale, ore is reported at that horizon in 28—galena alone in 10, blende alone in 7, and both galena and blende in 11. Nine of these 28 holes show also cuttings of ore at higher levels. In 8 the higher ore indicated is blende, and the remaining hole shows both blende and galena. In 19 holes, "mundic," or iron pyrites, is reported, associated with ore in 10 holes and occurring alone in 9 holes. The cuttings from 6 drill holes were assayed, the average blende content being 10.8 per cent and the average galena content being 3.3 per cent, or as 1:0.308.

If we take the production of the Granby district from 1893 to 1904, inclusive, as given by Buckley and Buehler,[1] and complete it by adding the production for 1905–6 from the Joplin statistics of weekly sales and the production for 1907–1912 from the annual volumes of "Mineral Resources of the United States," and if we calculate the metal content of the ores for the whole period by the average metal content (not recoverable zinc) for the years given in the "Mineral resources," we have a total of 85,000 tons of zinc and 13,338 tons of lead, a ratio of zinc to lead of 1:0.157, equivalent to a ratio of blende to galena of 1:0.122. On the other hand, if we take the total production of the Granby district from the time of the first discovery of lead up to 1893, as given by Winslow, and bring it to date, as above, we get a ratio of zinc to lead of 1:0.463, equal to a ratio of blende to galena of 1:0.359. If these ratios be compared with the ratio of blende to galena of 1:0.308, as shown by the assays of cuttings from the Chattanooga shale, it appears that the ore at the level of the shale is relatively richer in galena than the deposits worked during the last 18 years, and almost as rich in galena as the total ore produced to date. The high ratio of lead in the total production is the result of the preponderance of galena mined in the early years. The early mining in the Granby district was shallow and the ores were galena, cerusite, and calamine. Even now the output of calamine is two or three times as large as that of blende. The original deposits of sulphides in the open ground at the base of the Pennsylvanian shale were oxidized, the zinc being in part carried elsewhere and deposited as calamine, the galena and some cerusite remaining. In some places the galena was probably residually concentrated, as is pointed out by Winslow. And as mining went on and became deeper the ratio of zinc to lead steadily increased, as is shown by the following table:

Ratio of zinc to lead in ore produced at Granby, Mo., 1870–1912.

1870–1879	1 : 0. 84
1880–1892	1 : 0. 36
1893–1906	1 : 0. 22
1907–1912	1 : 0. 18

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[1] Buckley, E. R., and Buehler, H. A., op. cit., p. 4.

If the average rate of production and the average ratio of zinc to lead for the last 6 years be maintained for 15 years the ratio of zinc to lead in the total production at the end of that time will be just about that indicated by the assays of the deep drill cuttings. If the ratio of zinc to lead continues to increase it will, of course, not require 15 years to bring the average down to that of the drill cuttings.

The character of the ore solutions has been discussed rather fully in the preceding chapters. They were waters containing free carbon dioxide and hydrogen sulphide. Such waters may be very weakly acid, but they are not "acid solutions" in the sense in which that term is used by Buckley and Buehler in the foregoing quotation. They had in mind waters charged with sulphates and containing free sulphate radicle and free hydrogen ion; in other words, free sulphuric acid.[1] Waters weakly acid with carbonic acid and hydrogen sulphide would act practically as neutral waters. Therefore, according to Buckley and Buehler, "the galena should occur intimately mixed with sphalerite and pyrite in the primary deposits under the conditions cited. Furthermore, galena of undoubted primary concentration should occur down to the Devono-Carboniferous shales."

We have found, then, at Granby, the only place where the test can at present be fairly applied, that: (*a*) There is a persistent ore horizon at the level of the Chattanooga shale; (*b*) that galena and sphalerite both occur at this level; (*c*) that the relative proportions of lead and zinc at this horizon are practically the same as in the local deposits worked in the past and as likely to be worked in the future, for, although this conclusion may seem to be the result of pushing rather far the results of assays of cuttings for 6 drill holes out of 28, yet it is corroborated by the fact that of the drill holes showing ore, 21 showed galena at the shale horizon as against 18 that showed zinc; (*d*) that pyrite occurs with the galena and blende at the shale horizon; and (*e*) that of the holes showing ore at the deep horizon, 9 showed blende at higher levels as against 1 that showed lead. It would seem to the writer that the facts are about as near to the postulated conditions as one could reasonably ask.

ABSENCE OF ORE DEPOSITS, DOLOMITE, AND JASPEROID ABOVE THE CHATTANOOGA SHALE WHERE THAT FORMATION IS CONTINUOUS.

The Chattanooga shale, as has already been noted and as is shown on the map (Pl. III), is not widely distributed. Its northern edge in the Joplin region seems to pass near Miami, Peoria, and Granby, and to swing from Granby southeastward. The shale is not found at Quapaw, Galena, Joplin, Carthage, or Aurora. It is mapped at places southeast and southwest of Springfield by Shepard,[2] who also shows isolated outcrops north of Springfield. It apparently occurs also near Ash Grove, as is shown by the section of the Pennsylvania Co.'s shaft given by Winslow.[1] From Granby southeastward to White River it does not outcrop and its margin is not exactly known. It occurs near Eureka Springs, Ark., and outcrops in the bluffs at the headwaters of White River, between Eureka Springs and Fayetteville. It outcrops in a small area near St. Joe, Ark. It occurs west of Granby and Fayetteville wherever its horizon is at the surface, as far south as the lower stretch of Illinois River, in Oklahoma. The formation is therefore apparently persistent throughout that region.

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[1] See analyses of mineral and mine waters, quoted by Buckley and Buehler, op. cit., pp. 101-102.

[2] Shepard, E. M., A report on Greene County: Missouri Geol. Survey, vol. 12, pp. 67-71, 1898.

According to the artesian-circulation theory the distribution of the Chattanooga shale should show a clearly defined relation to the Joplin ore deposits. Where that shale is unbroken it should be impervious to ore solutions and should prevent their ascent into the Mississippian rocks above, and thus also prevent any ore deposition in those rocks. As a matter of fact, in the large area outlined on the map as underlain by continuous or unbroken shale there is no workable deposit of ore nor, so far as is known to the writer, any deposit that contains dolomite or jasperoid. The smaller patches may, of course, divert the ore solutions but can not prevent their ascent into the Mississippian. The single lead and zinc mine in the southwestern part of Washington County, Ark., is probably near the southern edge of the shale, which thins out toward the south and is absent in the small upthrown area a few miles northwest of Bunch, Okla. If a small deposit should at some time be found above the shale it would not contravene the foregoing statement, for a small deposit might conceivably be due to a local artesian circulation in the Boone formation.

PRESENCE OF ORE, DOLOMITE, AND JASPEROID ALONG THE SENECA FAULT WITHIN THE AREA UNDERLAIN BY THE CHATTANOOGA SHALE.

The writer has elsewhere[2] described the Seneca fault, which extends from a point several miles northeast of Spurgeon, Mo., southwestward to a point between Pryor and Choteau, Okla., a distance of about 70 miles. The fault is a double one, a long narrow block of Boone, Chester, and overlying rocks, from 200 to 1,300 feet wide having been let down into the Boone formation. The throw of the fault ranges from a few feet up to 100 feet or more. The northern border of the Chattanooga shale is crossed by the fault near Seneca and the territory southwest of that city traversed by the fault is underlain by the shale. The whole course of the fault between Seneca and Spurgeon is marked by prospect shafts which have located more or less ore, and considerable mining has been done at several places between these points and also southwest of Seneca as far as the Sycamore Creek district, a distance of 3 miles. The ore found along the fault is marked by the gangue minerals that are generally associated with it in the Joplin region—calcite, dolomite, and jasperoid. In the region southwest of the Sycamore district, however, for the remaining 50 miles over which the fault extends, neither dolomite, jasperoid, nor ore can be seen, although a few prospect openings lie along the course of the fault, and the fault zone, with its characteristic breccia, is exposed at several places in the bluffs of Neosho (Grand) River. Apparently the fault in this part of its course did not have sufficient throw to offset more than the thickness of the shale, or where the throw was greater than the thickness of the shale perhaps the shale was entrained in the fault plane and thus sealed the opening to the ascending circulating water. At any rate the Cambrian-Ordovician circulation does not seem to have made its way upward into the Mississippian rocks in this part of the course of the fault, for the breccia cement here instead of being the dolomite-jasperoid-ore cement found along the northeastern part of the fault, is exclusively calcitic, apparently having been derived by infiltration from the wall rock of Mississippian limestone.

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[1] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, p. 628, 1894.

[2] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, pp. 197-198, 1908.

The writer regards the absence of ore, dolomite, and jasperoid where the shale is continuous and their presence where its continuity is broken by the Seneca fault as conclusive proof that the ore and gangue were derived from solutions ascending from the Cambrian and Ordovician rocks.

HEAVIER ORE DEPOSITS AT THE NORTHERN MARGIN OF THE CHATTANOOGA SHALE.

A lens of Chattanooga shale intercalated between the Ordovician and the Mississippian would have the same effect on the artesian circulation as the "perched water tables" described by Veatch,[1] imposing certain irregularities on the artesian circulation, such as have been outlined in the chapter on underground circulation (p. 36). The large, continuous sheet of shale just described, however, not only partakes of the westerly dip of the uplift but lies on both its flanks and forms a cap over its southwestern axial prolongation. The intersection of the border of the Chattanooga shale with the inner margin of the Pennsylvanian shale on the south flank of the uplift is near Fayetteville, Ark., where the top of the shale lies

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[1] Veatch, A. C., Underground water resources of Long Island, N. Y.: U. S. Geol. Survey Prof. Paper 44, p. 57, 1906.

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about 1,000 feet above sea level, and the similar intersection on the north flank is near Miami, Okla., where the top of the shale lies about 400 feet above sea level. The relation thus described has a significant bearing on the extent of the ore deposits of the Joplin region, for it means that the Chattanooga shale slopes toward the Joplin district through most of the distance between Joplin and Fayetteville. The axis of the uplift passes between Fayetteville and Bentonville, as is shown by the deformation contours (Pl. IV). Water entering the Cambrian and Ordovician rocks on the higher central part of the uplift and flowing down the dome under artesian pressure will rise beneath the Chattanooga shale and tend to flow toward the highest part of the arched undersurface of the shale. In other words, the axis of the uplift thus becomes the main line of flow of the underground circulation in that direction. So too the Berryville-Joplin anticline will have a tendency to control the direction of the underground circulation. Having risen beneath the Chattanooga shale, which is continuous in the region about Fayetteville, Eureka Springs, Granby, and in the area farther west, the solutions have but two avenues of escape. Currents will be set up in these two directions and in the rest of the area the circulation will remain impounded. The direction of these two currents and their relations to the structural axis, to the distribution of the Chattanooga and the Pennsylvanian shales, and to the location of the mining districts of the Joplin region are indicated on the sketch map forming Plate X.

After the Pennsylvanian shales had been eroded away there would apparently be surface outlets on the south side of the axis near Morrow, Ark, and Bunch, Okla., for the water beneath the Chattanooga shale. Lead and zinc ores have been mined at Morrow.

Water circulating under the Chattanooga shale on the north side of the axis escapes only along the lower northern margin of the shale from Granby to Miami. It therefore flows beneath the Chattanooga toward that border, beyond which it ascends into the "open ground" of the Mississippian rocks and deposits its metals. The territory along the northern border of the Chattanooga shale is therefore favored by concentration in two directions. That is, the ore solutions in any sector of the dome will be concentrated in the subtending segment at the inner edge of the Pennsylvanian shale; but the solutions that flow out radially beneath the Chattanooga shale will be carried to the north edge of that shale, where they will rise and be added to the normal radial circulating water of the adjacent sector. It is significant that this area, between Granby and Miami, includes the principal ore-producing districts of the Joplin region.

DISTRIBUTION OF MINING DISTRICTS IN A CIRCLE CONCENTRIC WITH THE INNER EDGE OF THE PENNSYLVANIAN SHALE.

Almost every geologist who has described the ore deposits of the Ozark region has noted that the productive districts are distributed around the periphery of the uplift. Jenney[1] noted this distribution as follows:

> The ore deposits are confined to limited areas, distributed without apparent regularity over the uplifted regions but showing some tendency to group near the marginal belts rather than in the central plateaus.

Haworth[2] thus described the arrangement of the mining camps.

> It will be noted that all of the principal mining towns in the southwestern district, with the exception of Aurora and Wentworth, lie within a zone about 10 miles in width, which very closely parallels the axis of the Ozark area. This same condition is shown to be true elsewhere. The lead and zinc ores of Hickory, Benton, Morgan, Camden, Cole, and Miller counties in the central district, and of Franklin, Jefferson, Washington, Ste. Genevieve, St. Francois, and Madison counties in the eastern district, and the ore bodies near the boundary line between Arkansas and Missouri, on the south, all lie in this peripheral zone.

Keyes[3] emphasized the peripheral distribution of the productive areas about the uplift:

> The lead and zinc deposits of Missouri and Arkansas are not scattered promiscuously through the Ozark uplift but are confined to a well-defined belt of greater or less width which borders the basal margin of the dome and completely encircles it.
>
> The productive mineral-bearing belt is rather sharply delimited on its outer border by the margin of the coal measures. Its inner border is somewhat more irregular, owing to local peculiarities which need not be referred to in detail at this time. There are some unimportant deposits within the main ore ring in positions suggesting former locations of the belt, before the coal-measures margin had moved so far as it is at present down the slope of the dome.

Smith[4] likewise noted the circular zone of the mining districts:

> These four districts are arbitrarily chosen so as to include the chief ore-producing centers. If all the scattered deposits known in the region were included a continuous zone would be outlined, beginning with the southeastern Missouri district on the east, circling to the northwest, then to the south not far from the margin of the Ozark uplift, and finally eastward along the northern slopes of the Boston Mountains.

The peripheral arrangement of the productive districts about the Ozark uplift may be easily seen on the map (Pl. III). If individual occurrences of ore were shown the continuity of the belt would be even more striking. The one exception, already noted, is that the area underlain by a continuous sheet of Chattanooga shale contains no ore deposits. If the location of the ore bodies has been determined by the retreating edge of the Pennsylvanian shale, which formed the outward limit of the artesian circulation, as set forth in the preceding pages, the peripheral distribution is easily understood. No other explanation is evident.

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[1] Jenney, W. P., The lead and zinc deposits of the Mississippi Valley: Am. Inst. Min. Eng. Trans., vol. 22, p. 212, 1894.

[2] Haworth, Erasmus, Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, p. 104, 1904.

[3] Keyes, C. R., Geographic distribution of lead and zinc deposits of the Mississippi Valley: Eng. and Min. Jour., vol. 86, p. 1004, 1908.

[4] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 1, 1907.

This explanation is applicable also to the distribution of certain worked-out shallow lead deposits of the southeastern Missouri disseminated lead district, the location of which has been thus described by Buckley:[1]

> It is very significant that the shallow mines rarely occur in the Bonneterre except where the overlying Davis shale has been removed. It is also noticeable that these mines are chiefly near the contact of the Bonneterre dolomite and Davis shale.

The Davis shale of Buckley overlies the Bonneterre limestone and both, in the main, dip away from the St. Francis Mountains. The Lamotte sandstone, beneath the Bonneterre, is saturated with water under strong artesian head. Before the region was drained by mine pumps there must have been an artesian circulation in the Bonneterre as well as in the Lamotte, and the circulating water came naturally to the surface at the inner margin of Davis shale of Buckley, which he has described as an effective septum between the waters of the Bonneterre and the Potosi limestones. The area where the circulation reached the surface is marked here, as in the Joplin region, by ore deposits. That these deposits were small, and that many of the deeper and larger disseminated deposits are formed farther out, beyond the margin of what Buckley has called the Davis shale, and beneath the shale itself, does not militate against this view, as in the opinion of the writer the recurrent portion of the artesian path, that is to say, the return flow beneath the impervious cover is, in the Joplin region, the portion most effective for ore deposition. In that region deposits of lead and zinc ores occur beneath the Pennsylvanian shale cover several miles back from its margin.

Winslow,[2] who postulated descending or laterally moving solutions to explain the lead and zinc deposits elsewhere in Missouri, appealed to a distinctly artesian circulation to account for the deep disseminated lead deposits of southeastern Missouri, as the following extract will show:

> The numerous vertical crevices furnished channels for the flow of the solutions. The sheets of galena frequently found in these crevices prove that the solutions followed them. These were sufficient to supply the ore of higher-lying disseminated bodies. The contraction and disappearance of the crevices with depths make them inadequate for the deep deposit such as prevail along Flat River. For these ores we are inclined to refer to the underlying sandstone, which is in close proximity, as the solution carrier. This is saturated with water, much of which flows directly from decomposing crystalline rocks. The sandstone itself contains particles and fragments

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[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, 2d ser., vol. 9, p. 229 [1909].

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 486-487, 1894.

of these rocks, which must hold more or less of the metals. A downward flow of water toward Flat River and Bonne Terre is induced by reason of the slope of the Archean floor, and also probably by the Farmington anticline to the east which we have described. The water is thus under pressure sufficient for it to rise up through the limestones, and where suitable physical and chemical conditions are reached the deposition of the ore will take place.

In fact, Buckley [1] attributes the disseminated lead deposits in part to artesian solutions:

> The disseminated ore bodies were in part the result of the abstraction of lead from waters circulating along channels and bedding planes in their journey from the surface to the sand, and in part from solutions, under hydrostatic pressure, which rose along channels which extend upward into the dolomite from the underlying sandstone. These channels, in some instances, may have reached to the top of the Bonneterre and the small irregular disseminated ore bodies of the upper levels may have been formed by these solutions.

It would be difficult indeed to explain, otherwise than by ascending solutions, the deposition of such ore bodies as Nason [2] describes in this region as follows:

> At two shafts with which the writer is well acquainted, immediately under the slates [Davis shale of Buckley] was a larger or flat channel from which a large quantity of surface [coarsely crystallized] lead was taken.

In the upper Mississippi Valley region, according to Van Hise,[3] the Maquoketa ("Cincinnati") shale forms the upper limit of the artesian circulation. Here also the lead and zinc deposits are inside but adjacent to the inner margin of the shale.

Similar relations of the ore deposits to an overlying shale cover are shown in many places on the map of the eastern part of the United States (Pl. XI).

LEAD AND ZINC DEPOSITS AT GREAT DEPTHS.

Cuttings from deep drill holes made at many places in the Joplin region, in Kansas northwest of the Joplin region, and elsewhere in the Mississippi Valley contain sphalerite and galena. Some of these cuttings were raised from depths greater than those to which it may reasonably be assumed that descending surface waters penetrate, and some of them were taken from points beneath very considerable thicknesses of Pennsylvanian shale. Zinc ore is reported in chert in the cuttings of a well at Stone City, Kans., at a depth of 591 feet, 220 feet below the base of the Pennsylvanian shale.[4] The writer is informed by William Waugh, one of the drillers of the Stone City

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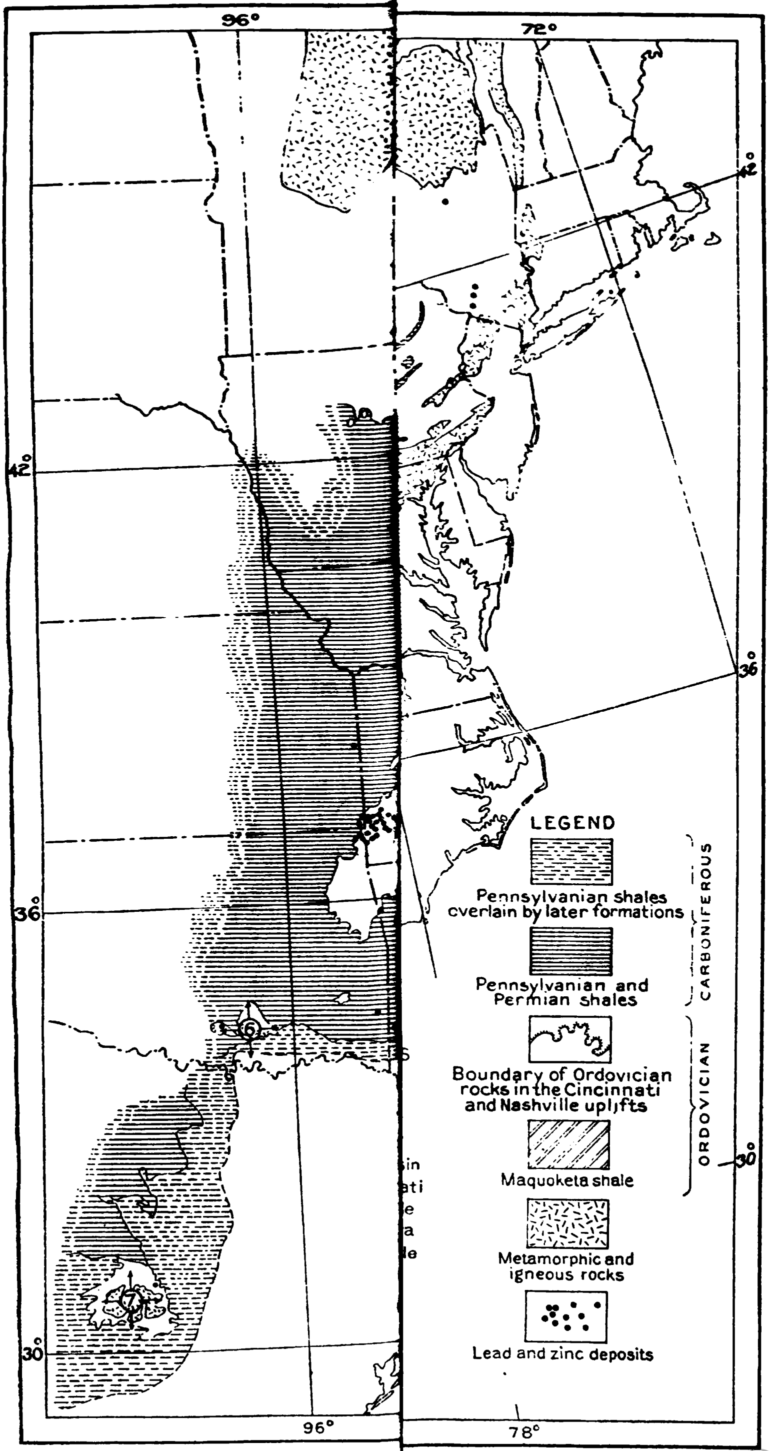
[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties: Missouri Bur. Geology and Mines, vol. 9, p. 234 [1909].

[2] Nason, F. L., The disseminated lead deposits of southeast Missouri: Eng. and Min. Jour., vol. 73, p. 480, 1902.

[3] Van Hise, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng. Trans., vol. 30, pp. 143-150, 1901.

[4] Haworth, Erasmus, Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, p. 63, 1904.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ORDOVICIAN
Metamorphic and igneous rocks
Lead and zinc deposits

MAP SHOWING RELATION OF O UPLIFTS AND MARGINAL

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well, that cuttings from other wells which he has drilled in the vicinity of Pittsburg, Kans., have shown galena and sphalerite taken from about the same depth as in the Stone City well, and that the showing of ore at some places would be considered good enough to justify sinking a shaft had it been found in the Joplin district and at shallower depths.

A number of deep holes drilled in the Joplin district for water have struck deposits of zinc and lead at depths between 300 and 800 feet. The ore-bearing bed in the Granby district at a depth of about 300 feet has already been noted.

J. A. Udden records[1] the occurrence of sphalerite in the cuttings from the Carbon Cliff well, 10 miles east of Rock Island, Ill., at a depth of more than 700 feet in the Galena limestone. He also notes[2] the presence of sphalerite in cuttings from a well at Peoria, Ill., in limestone and shale, correlated with the Kinderhook, at a depth of 699 feet.

These occurrences of lead and zinc and the one struck in the drilling at Belle Isle, La., to be described later, are easily comprehensible in the light of the artesian-circulation theory and seem to be logical consequences of such a circulation of the ore-bearing solutions, but it is extremely unlikely that solutions moving directly downward from the surface could have deposited the sulphides.

ORE DEPOSITS BENEATH PENNSYLVANIAN SHALE.

The zinc and lead ores at Miami, Okla., are in sandstone of Chester age that is overlain by Pennsylvanian shale and in the cherty Boone limestone that lies directly beneath the ore deposits in rocks of Chester age. The sandstones associated with the ores are impregnated with bitumen, which causes trouble in concentrating the ores.[3] The ores have not been directly oxidized although they have been affected somewhat by solution, as is shown by the occurrence of etched crystals of galena and sphalerite in several mines. The work of draining the mines at Miami was heavy from the very beginning of mining. One of the effects of the pumping was to dry up a large sulphur spring at a point not far from the end of the long run in which the principal ore was found. This spring was well known, because the bog around it had yielded a large collection of bones of prehistoric animals, which testified to its long existence.

The mine water at Miami first pumped was highly charged with hydrogen sulphide, and in early days, when the mine drifts were small, the gas was so strong as to affect the eyes of the miners, who could therefore work only in half-day shifts, or, when the gas was very strong, in half-hour shifts. As mining was continued and as the underground workings were made larger, the hydrogen sulphide was hardly noticeable except in new and small drifts at some distance from the old workings, as described on pages 227–228. Similar occurrences of hydrogen sulphide gas in mine drifts in Kentucky have been reported by A. M. Peter.[1]

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[1] Udden, J. A., An account of the Paleozoic rocks explored by deep borings at Rock Island, Ill., and vicinity: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 836, 1896.

[2] Udden, J. A., Artesian wells in Peoria and vicinity: Illinois State Geol. Survey Bull. 8, p. 322, 1907.

[3] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, p. 209, 1908.

According to the artesian-circulation theory of the genesis of the Joplin ore deposits, the first water struck in mines beneath the Pennsylvanian shale—that is, the water that comes into the mines when they are first opened, really the ground water of the region beneath the shale—should resemble the water of the original artesian circulation, which is represented by the waters of the deep wells in the Pennsylvanian area west of the Joplin region, wells that draw their supply from the Cambrian and Ordovician rocks. After the water table has been so much lowered by pumping that the water draining the surface strata passes downward to the mine drift, the mine waters are entirely different from those first pumped. Very generally in the Joplin region the water pumped from a mine just opened at some distance from older mines is at first potable. Later, owing to oxidation of ores in the upper part of the mine, it becomes unpalatable and even strongly acid.

The analyses of deep-well waters already presented show that the water of the original circulation was alkaline-saline and contained free carbon dioxide and hydrogen sulphide. The analyses of the Miami mine waters, also presented herein, show that they are very similar to the waters of the deep wells. The abundance of hydrogen sulphide in the waters of the Miami mines has already been noted.

The Miami mines are the only deposits beneath the Pennsylvanian shale so far worked in the Joplin region. The mine waters here are not only of the general character demanded by the artesian theory but differ from all other mine waters in the district and even from the waters of the interior deep wells, resembling closely the waters of the deep wells at the border of the region. A sample of water from the Church mine, collected in 1911 (No. 18 in the table of analyses, p. 137), yielded on analysis a trace of zinc. An analysis of the water from the Chapman & Lennan mine, collected in September, 1912, when the mine was opened (see No. 30 in the table) yielded no zinc, but both this and the Church mine water contain hydrogen sulphide and correspond closely with the waters of the deep wells at the border of the region, among which they fall in the synoptical table (pp. 149–150). A second analysis of the Chapman & Lennan mine water (No. 71), made in December, 1912, after three months' steady pumping had drained all the surrounding mines, shows plainly the influence of surface conditions in the doubled quantity of calcium bicarbonate. The oxygen and carbonic acid brought in by mine ventilation and the influx of some surface water were factors in the change in the water. According to the artesian-circulation theory the water first pumped from this mine represents the water of the original ore solution and the water pumped later represents a water that has yielded its metals and that has been contaminated to a certain extent by surface waters.

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[1] Kentucky Agr. Exper. Sta. Eighteenth Ann. Rept. (for 1905), p. 229 [1906]; Nineteenth Ann. Rept. (for 1906), p. 274 [1907].

The writer has already suggested on page 34 that there is a reverse current beneath the edge of the Pennsylvanian shale bordering the artesian area. The occurrence of ore at Miami and its reported occurrence in Kansas several miles back from the margin of the shale show that the reverse circulation reaches back beneath the shale for 5 or 6 miles at least from the border. Farther back, beyond the reach of this subshale circulation, the ground water must be impounded and practically stagnant. The Pennsylvanian shale in this region of subshale circulation lies on the old karst topography of pre-Pennsylvanian time. The Mississippian limestone and chert rocks, which had been fashioned into the karst topography, constituted an eminently suitable site for ore deposition in the channels, cavities, and breccias which resulted from solution of the limestone. Here the slow-moving metal-bearing solutions with dissolved carbon dioxide and hydrogen sulphide would be under favorable conditions to permit the escape of the carbon dioxide with resulting precipitation of sulphides by the hydrogen sulphide. Exactly similar conditions must have obtained beneath the marginal zone of the shale during its entire retreat down the slope of the dome. It is believed that most of the open-ground deposits in the region were deposited in a position analogous to these deposits beneath the Pennsylvanian. The open-ground deposits are very commonly associated with shale patches which represent the "roots" of the downward extensions of the shale as deposited in the depressions of the karst topography.

BITUMEN AT THE BASE OF THE PENNSYLVANIAN SHALE.

At a place known as Tar Spring, on Tar Creek, about 6 miles north of Miami, Okla., a heavy bitumen oozes in considerable quantity from the bank of the creek at the contact of the Pennsylvanian (Cherokee) shale and the lower rocks. In the mines at Miami the sandstones and limestones of Chester age at the same geologic horizon, the base of the Pennsylvanian shale, are impregnated with bitumen, which, as has already been noted, interferes seriously with the concentration of the lead and zinc ores occurring in the same sandstone. In the same mines bitumen also oozes from crevices in chert of the Boone formation below the Chester rocks. The bitumen sometimes interferes greatly with prospecting by the churn drill. Bitumen occurs in limestone of Chester age at the base of the Pennsylvanian shale just west of Afton, Okla., and also in pockets in the Boone formation in association with the ore deposits of the Joplin region generally.

When petroleum is forced through a bed of shale it is fractionated into its lighter and its heavier components, the lighter parts passing through the shale and the heavier parts—that is, the bitumen—remaining behind. If the current carrying the petroleum from which the bitumen was derived was ascending, the bitumen would have been left behind at the place where it is now found—the base of the Pennsylvanian shale. Water ascending under artesian pressure may drive oil out of shaly formations, but oil can not possibly go downward into shale, driving out water before it; and if it could, it would leave the fractionated bitumen at the top of the shale. Hence the circulating water that left the bitumen, which is closely associated with the ores at Miami, was ascending, a conclusion confirmed by the analyses of the bitumen. On the 240-foot level of the Lennan Zinc & Lead Co.'s mine in the Miami district the "tar" seeps from the chert wall of the drift and forms a pool containing several barrels. A sample of this bitumen and a sample of a similar bitumen found below the Pennsylvanian shale in a bore hole in the northern part of the district, near the Kansas-Oklahoma State line, about 8 miles west of Baxter Springs, Kans., were analyzed by David T. Day, of the United States Geological Survey, who makes the following report showing the result of his analysis:

> I have examined the two samples of "tar" from the Miami mining district of northeastern Oklahoma. The examination shows that these tars contain only about 8 per cent of hard asphalt and would be classified as asphaltic oils, and that they consist entirely of unsaturated hydrocarbons. Such hydrocarbons would not diffuse readily through shales or other very close grained rocks. The unusual fact that they contain no saturated hydrocarbons whatever indicates that a proportion of saturated hydrocarbons has escaped by diffusion into the close-grained rocks, leaving this material as a residue. This is what would necessarily take place with a crude oil, containing both saturated and unsaturated hydrocarbons, in contact with Pennsylvanian shale, and would entirely accord with the idea you express in your letters as to the fractionation of this petroleum at the base of the shale.

THE PLEASANTON CIRCLE.

According to Haworth,[1] a considerable quantity of lead ore and some zinc ore has been mined near Pleasanton, Linn County, Kans., about 50 miles within the border of the area of Pennsylvanian shale. The ores are said to occur in a circular disturbed area in the shale, about 50 feet in diameter. At this place there were three periods of mining activity, during one of which, about 1873, a shaft is reported to have been sunk to a depth of 250 feet. Between 1900 and 1901 another shaft was sunk to a depth of more than 100 feet. The base of the Pennsylvanian shale in that region is reached at a depth of about 500 feet. During the last period of mining about 15 tons of lead ore was taken from depths of 65 to 85 feet. In all perhaps 50 tons of ore was raised, mostly galena.

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[1] Haworth, Erasmus, Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, pp. 69-70, 1904.

Haworth says:

> The galena was of a high grade of purity, was not weathered or oxidized in the least, and produced brilliant surfaces on the crystalline faces, approximating in brilliancy fresh cleavage surfaces. This implied recent deposition, or at least a total absence of an approach toward disintegration or weathering. There was no indication of spring water or artesian water rising in the ore chimney, but everything implied that the water present was surface water working downward in a normal condition.

This appears to be a "circle deposit" strictly analogous in structure to the circle deposits of the Joplin district, except that both the center (or core) and the side walls are shale, whereas in the Joplin district the core may be shale but the side walls are invariably chert and limestone. The circles of the Joplin region have originated by the dropping down of the central area, owing to solution of the underlying limestone. The shale center in some circles has thus been displaced as much as 200 to 250 feet. When the circles were first formed, before the Pennsylvanian (Cherokee) shale was eroded from the Joplin region, their upward extensions consisted of shale both as to core and side walls, and they must have presented much the same appearance as the Pleasanton circle. In order to produce this appearance the shale in the circle need not drop as much as 500 feet, of course; a drop of a small part of that distance would probably cause a break that would reach to the surface. The karst topography of the Mississippian limestone on which the Pennsylvanian shales were laid down doubtless extended as far northward as Pleasanton, and the conditions were probably favorable to the formation of such circles.

In the absence of any other explanation of the local disturbance of the shale in the Pleasanton circle, and in view of what has been said above, it seems reasonable to conclude that this circle had an origin similar to that of the analogous circles in the Joplin district. If so, this circle reaches also to the Mississippian limestones and the way would be open for the ascent of the artesian water, which might be expected to deposit the metals in the brecciated shale just as similar waters rising through bore holes deposit the metals in the waterworks reservoirs in the same region. Haworth[1] says there is no evidence that the circle has been filled with artesian water. In the absence of an analysis of the water, it is not clear what evidence would show that the waters were or were not artesian, unless it be a flow above the surface. But the elevation of Pleasanton, 862 feet above sea level, is probably too great to permit a flow at the surface in that region at the present time. On the other hand, the absence of oxidation of the sulphides indicates that they have not been subject to the action of surface waters.

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[1] Haworth, Erasmus, op. cit., p. 70.

Finally, if the disturbance does not reach the Mississippian and if there is no escape for the surface water in that direction, it is hard to see why there should be sufficient drainage toward this chimney or natural well in the shale to concentrate the metals from the surrounding shale. It seems more reasonable to think that the surface water would fill the chimney up to the water table, its level remaining stationary at that point, whatever rainfall was added flowing off laterally down the slope of the water table. Thus there would be no appreciable drainage from the surrounding region to the chimney and little possibility for the concentration of ores in it.

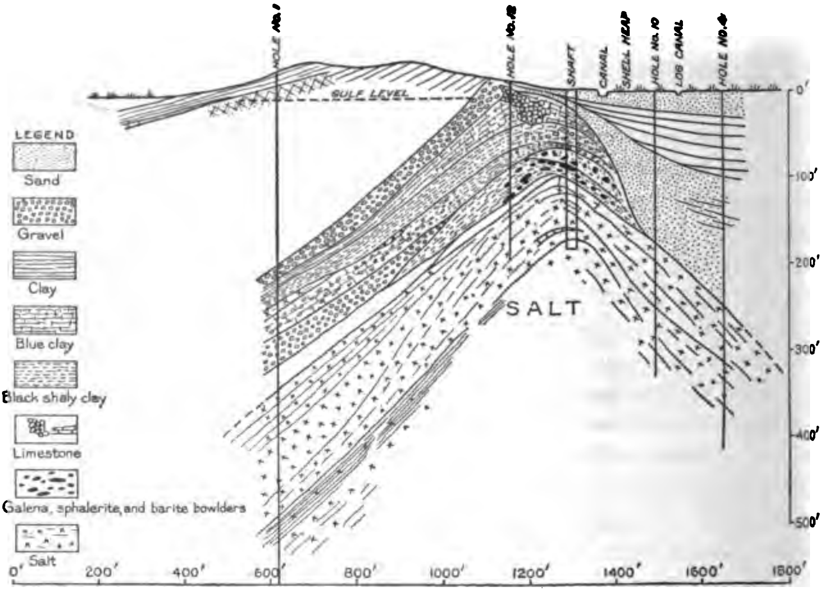

FIGURE 8.—Cross section of Belle Isle, La. (After Veatch, Louisiana Geol. Survey Ann. Rept. for 1899, p. 228.)

GALENA AND SPHALERITE IN LOUISIANA SALT MOUNDS.

Veatch[1] notes the presence of fairly large masses of galena, sphalerite, pyrite, chalcopyrite, and barite in clay strata penetrated at a depth of 63 to 68 feet by a salt shaft sunk on Belle Isle. The structure of Belle Isle (fig. 8) is very sharply anticlinal and the sulphides were found at the crest of the anticline, 45 feet above the first showing of salt. Harris[1] gives the log of a deep drill hole sunk about 100 feet south of the shaft. In this hole pyrite was found in shale at 100 feet and in limestone at 2,112 feet, and galena, chalcopyrite, and pyrite were found in rock salt at 2,520 to 2,606 feet. Small quantities of gas and oil were struck at several horizons, as well as deposits of sulphur, gypsum, and anhydrite. The sulphides thus occur to a greater or lesser extent in association with deposits of salt, gypsum, dolomite, barite, sulphur, oil, and gas. The sulphides consist of aggregates of sharp, unworn crystals, which evidently have not been transported but have been segregated in place in the clays. Shell beds involved in the dome structure contain shells of species now living in the Gulf of Mexico, a fact which seems to show that the period of the uplifting was Pleistocene or Recent. The country about Belle Isle is a salt-water marsh. From the surface of the marsh to a depth of 100 feet or so there are clays; below this come 300 to 400 feet of gravels, in which there is fresh water under artesian pressure. Therefore the sulphides and salt can hardly have been concentrated laterally from strata outside the present area of the dome since the dome was formed. Before the dome was formed the clays in which the sulphides are found were probably spread out horizontally some distance below sea level, and it is difficult to understand how the sulphides could have been segregated in that position. Nor is it easy to see how they can have been leached from the clays making up the upper part of the dome and deposited by descending waters. The position of the sulphides at the crest of the anticline indicates rather that they were deposited by ascending solutions.

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[1] Veatch, A. C., The Five Islands: Louisiana Geol. Survey Ann. Rept. for 1899, p. 225 [1900].

Fenneman[2] cites the abnormally high temperature of the waters associated with the oil and gas and salt domes of the Coastal Plain as evidence that they are ascending waters. He also notes that some of the waters in these domes are as saline at depths of 100 or 200 feet as the waters of wells 2,000 or 3,000 feet deep elsewhere in the Coastal Plain, and this he cites as further evidence of their ascension.

Harris accounts for the dome structure as the result of upward thrust due to the growth of crystals, chiefly of salt, in masses below, the salt crystallizing out of saline waters rising under artesian pressure. If the several domes be plotted by dots on a map and these dots connected by lines, the lines, according to Harris,[3] represent series of northeast-southwest and northwest-southeast parallel faults, at the intersections of which the waters under artesian pressure found a readier outlet to the surface. He holds that these artesian waters were undoubtedly derived from the gulfward-sloping formations of the Coastal Plain of the Mississippi embayment. He points out that the great Balcones fault in Texas has a southwest-northeast course, and that the Red River fault of Texas and the Alabama Landing fault of Louisiana have northwest-southeast courses, both systems being roughly parallel to the corresponding sets in the theoretical systems of faults. Some years ago Branner[1] discussed the relation of the Balcones fault of Texas and of other faults in Arkansas to the western margin of the Mississippi embayment and the relation of faults in Alabama to the southeastern margin of the embayment. The views of Branner and Harris thus in a way supplement each other.

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[1] Harris, G. D., Oil and gas in Louisiana, with a brief summary of their occurrence in adjacent States: U. S. Geol. Survey Bull. 429, pp. 44-45, 1910.

[2] Fenneman, N. M., Oil fields of the Texas-Louisiana Gulf Coastal Plain: U. S. Geol. Survey Bull. 282, pp. 120-121, 1906.

[3] Harris, G. D., Rock salt, its origin, geologic occurrences, and economic importance in the State of Louisiana: Louisiana Geol. Survey Bull. 7, pp. 75-82, 1908.

Hill,[2] citing immense springs which rise along the Balcones fault, had previously attributed the salt, sulphur, dolomite, gypsum, and other deposits of the mounds to replacement of limestone by artesian flows from the water-bearing beds of the Cretaceous which rise along faults and transport, besides the substances mentioned, gas and petroleum. It was early suggested that the domes were caused by the intrusions of volcanic plugs, and Washburne[3] has further suggested that emanations from such intrusions which have not reached the surface have been instrumental in the formation of the associated deposits of salt, dolomite, and gypsum. On the other hand Ordóñez[4] holds that the connection between the oil and the volcanic rocks in Mexico is exclusively mechanical, having nothing to do with the origin of the oil, which is believed to be purely organic. Christie[5] quotes the explanation of Arrhenius that such deposits of salt as those of the mounds are due to gravity—the salt, being lighter than the overlying rocks and plastic under pressure, is squeezed upward along lines of weakness. No matter which of the theories proves to be correct, the postulated conditions provide openings for the ascent of the artesian waters of the Gulf Coastal Plain formations.

The waters that deposited the salt at Belle Isle deposited also sulphur, gypsum, limestone, and dolomite. Hence the waters were alkaline-saline sulphureted waters carrying a notable content of magnesium. This is likewise true of the deeper waters of the Joplin region. The substances brought in by the solutions that formed the salt domes are lead, zinc, iron, and copper sulphides, salt, gypsum, barite, sulphur, dolomite, oil, and gas. Those brought in by the solutions that deposited the Joplin ores are lead, zinc, iron, and copper sulphides, dolomite, and a little barite. Barite, however, is very plentiful in the central Missouri lead and zinc mines and in the shallow lead mines of southeastern Missouri. The general presence of bitumen in the Joplin district and the "tar" in the ores at Miami, Okla., have been noted on pages 205–206. Moreover, the deep waters of the Joplin district, especially those impounded beneath the Pennsylvanian shales, are relatively rich in salt, sulphureted hydrogen, and calcium sulphate. The very close similarity of the deposits and the artesian waters of the saline domes to those of the Joplin region indicates similarity of origin.

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[1] Branner, J. C., The former extension of the Appalachians across Mississippi, Louisiana, and Texas: Am. Jour. Sci., 4th ser., vol. 4, pp. 362–365, 1897.

[2] Hill, R. T., The Beaumont oil field, with notes on other oil fields of the Texas region: Franklin Inst. Jour., vol. 154, pp. 273–281, 1902.

[3] Washburne, C. W., Chlorides in oil field waters: Am. Inst. Min. Eng. Trans., vol. 48, pp. 692–693, 1915.

[4] Ordóñez, Ezequiel, The oil fields of Mexico: Am. Inst. Min. Eng. Bull. 94, p. 2532, 1914.

[5] Christie, W. A. K., Notes on the salt deposits of the Cis-Indus Salt Range: India Geol. Survey Records, vol. 44, pt. 4, p. 258, 1914.

LEAD AND ZINC DEPOSITS ASSOCIATED WITH OTHER GEANTICLINAL UPLIFTS AND MARGINAL SLOPES OF THE CENTRAL VALLEY OF THE UNITED STATES.

DEPOSITS IN UPLIFTED AREAS IN CENTRAL VALLEY.

GENERAL CONDITIONS IN THE UPLIFTED AREAS.

The explanation of the genesis of the Joplin ore deposits set forth in the preceding pages, if true, should be of general application, and wherever beds of limestone and dolomite containing disseminated metals and overlain by an impervious cover have been elevated into a geanticlinal or sloping position there we should look for the development of an artesian circulation and of a tendency to segregation of the metals. Whether the masses produced by such segregation shall be large enough to be called ore deposits will depend on several conditions, among others the quantity of disseminated metals available for concentration, the competency of the circulating water to carry them, the presence of a physical environment favorable for their segregation, and the duration of the period of circulation. If, for example, the metal-bearing solutions rose against an impervious shale cover and found no fractures or openings other than the natural pore spaces and the joints of the rocks, ore would probably not be deposited with the same facility or in the same quantity as in the open ground at the base of the Pennsylvanian shale in the Joplin district.

In the central valley of the United States, besides the Ozark region, several areas of low, flat uplift offer the requisite structural conditions for testing the theory. They are indicated on the accompanying sketch map (Pl. XI), which shows the outcropping formations at the crest of each area, the inner border of the impervious cover, and the mining districts, or, if the deposits are not of that order of magnitude, the individual occurrences of ore.

WISCONSIN UPLIFT.

The chief of these areas is the Wisconsin uplift, in which the essentials of the artesian-circulation theory were first worked out by Van Hise.[1] The elevated area of crystalline rocks in north-central Wisconsin is flanked by sedimentary rocks, which dip gently to the southwest, south, and southeast. The lead and zinc deposits are found in dolomitic limestones that are capped by the Maquoketa shale, both of Ordovician age. According to Van Hise, the artesian circulating water that deposited the ores was limited above by the impervious Maquoketa shale. The main deposits are limited to the area embracing the southwestern part of Wisconsin and the contiguous parts of Illinois and Iowa, but smaller, isolated deposits stretch away for some distance in the direction of the Maquoketa border to the northwest, and also to the east.

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[1] Van Hise, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng. Trans., vol. 30, pp. 142–150, 1901.

CINCINNATI UPLIFT.

The Cincinnati uplift is another area that exhibits the proper structural conditions to furnish an artesian circulation. Calcareous shales and shaly limestones of Ordovician age form the center of the area and are overlain by Silurian and Devonian limestones, these, in turn, being overlain by Devonian and Carboniferous shales. The rocks of the central or Blue Grass region of Kentucky are fairly rich in lead, and numerous veins of galena, with barite and fluorspar gangue, are scattered over the region.[1] This fact harmonizes with the place relations of the metals to the center of the radial circulation, as pointed out on page 177. Deposits of zinc are found in Lewis, Rowan, and adjoining counties on the southeastern border of the uplift, and smaller deposits are found on the western border. The deposits in Lewis and Rowan counties have lately been examined for the Kentucky Geological Survey by Fohs,[2] who has kindly indicated for the writer the location of a number of other deposits not within the area discussed in his report. The ore is found in limestone of Niagara age, and lies within 10 miles of the border of the Pennsylvanian shale. In general, the northern part of this uplift, in Ohio and Indiana, does not seem to have been the site of a metalliferous circulation. The outcropping rocks differ from those in the Blue Grass region in that they consist of shales of the Richmond formation, which, in addition to being poorer in the metals, have afforded a poor artesian circulation.

NASHVILLE UPLIFT.

The Nashville uplift, the southern continuation of the Cincinnati anticline, is characterized by the same structural relations and practically the same stratigraphic relations as the Cincinnati uplift. Numerous deposits of lead are known in the central region of Tennessee, and some of them have been mined, as is noted by Nelson.[3]

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[1] Miller, A. M., The lead and zinc bearing rocks of central Kentucky, with notes on the mineral veins Kentucky Geol. Survey Bull. 2, pp. 25-35, 1905.

[2] Fohs, F. J., Kentucky Geol. Survey Rept. of Progress for the years 1910 and 1911, pp. 6-7, 1912.

[3] Nelson, W. A., Notes on lead in Tennessee: Resources of Tennessee, vol. 2, No. 3, pp. 100-117, Tennessee Geol. Survey, 1912.

Deposits of zinc occur in the area, but information is not at hand as to their location. The Nashville uplift extends into the northern part of Alabama, where lead has been mined near Guntersville, in Marshall County, and near New Market, in Madison County.

KENTUCKY-ILLINOIS FLUORSPAR DISTRICT.

Although the Kentucky-Illinois fluorspar district is not an uplift, it is so related to the Cincinnati and Nashville uplifts, both in its structure and the character of its ore deposits, as to bring it strictly within the limits of this discussion.

The lead and zinc deposits of the Kentucky-Illinois fluorspar district, because of their common association with a fluorite gangue and their occasional association with igneous dikes, are regarded by some writers as genetically distinct from the other deposits of the Mississippi Valley. Emmons,[1] writing in 1892, before any exposures of igneous rocks were known in Illinois, says that, as far as the facts go, they point to the derivation of the fluorspar and the metallic minerals from the surrounding limestone. Bain,[2] in 1904, after numerous dikes and sills of mica-peridotite and lamprophyre had been discovered in Kentucky and Illinois, declared for the igneous origin of the deposits, maintaining that they were derived chiefly from hot solutions given off by the parent magma of the dikes and basing his conclusions on the association of antimony with the lead; on the argentiferous character of the galena, which has an uncommonly high silver content for Mississippi Valley lead ores; on the enormous quantity of fluorspar as contrasted with that in other lead and zinc districts in the Mississippi Valley, which do not contain any fluorspar; on the deposition of the ore in true fissure veins; and, finally, on the occurrence of igneous rocks in the vicinity of the ore deposits. Bain has strongly reaffirmed this view recently.[3] Smith,[4] noting the igneous dikes and the deep-seated fissures which they indicate, thought it probable that the ore and gangue minerals were dissolved from the rocks below the Carboniferous system by thermal circulating underground waters which ascended through fissures to the Mississippian rocks, where the ores were deposited. Fohs[5] accepts the theory of the igneous origin of the deposits as best explaining their peculiar features.

The Kentucky-Illinois fluorspar district (see Pl. XI) occupies a position midway between the Nashville uplift and the Ozark uplift. These uplifts were probably once connected by a structural ridge. A broad structural ridge trends northwestward from the St. Francis

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[1] Emmons, S. F., Fluorspar deposits of southern Illinois: Am. Inst. Min. Eng. Trans., vol. 21, p. 52, 1893.

[2] Bain, H. F., The fluorspar deposits of southern Illinois: U. S. Geol. Survey Bull. 255, pp. 61–67, 1905.

[3] Bain, H. F., Min. and Sci. Press, vol. 108, pp. 299–300, 1914.

[4] Ulrich, E. O., and Smith, W. S. T., The lead, zinc, and fluorspar deposits of western Kentucky: U. S. Geol. Survey Prof. Paper 36, pp. 150–154, 1905.

[5] Fohs, F. J., Fluorspar deposits of Kentucky: Kentucky Geol. Survey Bull. 9, pp. 61–63, 1907.

Mountains toward the central Missouri district and a similar ridge extends southeastward from the St. Francis Mountains and is cut off by the Mississippi embayment. If continued in this line, it would join the Tennessee uplift and would put the Kentucky-Illinois fluorspar district on the north slope of this ridge, with the rocks dipping northward toward the Pennsylvanian shale. Prior to the formation of the Mississippi embayment this district, so far as structure, relation to the Pennsylvanian, and artesian possibilities are concerned, would be in a position analogous to the mining districts of the Ozark uplift, but since the formation of the embayment, which probably antedated the ore deposition, there has been no large expanse of higher rocks to the south and west to furnish an artesian circulation. It seems to the writer, however, that water falling on the west side of the Cincinnati uplift and on the northwest portion of the Nashville uplift and entering into the flow down the slopes of those uplifts beneath the Ordovician and Devonian shales must to some extent escape upward in the intensely faulted region of the Kentucky-Illinois district. There are no igneous rocks near the Cincinnati or Nashville uplifts, except the peridotite dikes of Elliott County, described by Diller,[1] which are 100 miles from the center of the Cincinnati uplift and on its eastern slope, so that they can not have contributed to the waters which deposited the ores of the Kentucky-Illinois fluorspar district. Veins containing galena or sphalerite, with a gangue of calcite, barite, or fluorspar, are common in both uplifts, as noted by Miller[2] and by Nelson.[3] Emmons[4] found an appreciable quantity of fluorine in limestone collected at some distance from any fluorspar deposit in southern Illinois and Smith[5] gives an average of 0.08 of 1 per cent in 3 samples of limestone not near fluorspar deposits in western Kentucky. Finlayson[6] found fluorine in each of four samples of limestone tested for that element. Miller does not mention dolomite among the gangue minerals in the veins of central Kentucky, nor does Nelson list dolomite as occurring with galena in middle Tennessee. It has already been noted that the waters of central Kentucky are alkaline-saline carbonated and sulphureted and commonly zinciferous. No doubt the waters of the Nashville uplift are similar. Carles has shown (see pp. 55–56) that carbonated waters can dissolve and transport compounds of barium, strontium, and fluorine. If the water of an artesian circulation could find its way from these uplifts to the faults of the fluorspar district, it would beyond question be capable of forming both the ore deposits and their unusual gangue. Water falling on the portions of the uplifts indicated must in part enter the underground circulation of the Ordovician limestones. These limestones are overlain by shaly Ordovician formations, and still above by the Chattanooga shale. These shale formations will prevent the upward escape of the circulating water, which must therefore seek to ascend through the complex system of fractures and faults in the western Kentucky area. The fact that this area lies much lower than the intake areas in the uplifts makes such escape possible; and furthermore, as the only avenue of escape of waters from the considerable areas indicated, it necessitates a very considerable concentration of the circulating water at this point, with probable resulting segregation of its mineral content.

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[1] Diller, J. S., Peridotite of Elliott County, Ky.: U. S. Geol. Survey Bull. 38, pp. 9–10, 1887.

[2] Miller, A. M., The lead and zinc bearing rocks of central Kentucky, with notes on the mineral veins: Kentucky Geol. Survey Bull. 2, pp. 25–35, 1905.

[3] Nelson, W. A., Notes on lead in Tennessee: Resources of Tennessee, vol. 2, No. 3, pp. 100–117, Tennessee Geol. Survey, 1912.

[4] Emmons, S. F., Flourspar deposits of southern Illinois: Am. Inst. Min. Eng. Trans., vol. 21, p. 52, 1893.

[5] Smith, W. S. T., The lead, zinc, and fluorspar deposits of western Kentucky: U. S. Geol. Survey Prof. Paper 36, p. 152, 1905.

[6] Finlayson, A. M., Problems of ore deposition in the lead and zinc veins of Great Britain: London, Geol. Soc. Quart. Jour., vol. 66, p. 300, 1910.

Quantitative analyses are not at hand to determine whether or not the underground waters of the district are deep seated in origin. Burk [1] has pointed out that "springs of water heavily charged with hydrogen sulphide are found along the principal lead and zinc sulphide deposit in the Columbia vein"—one of which is the Crittenden Spring. The water from this spring was qualitatively analyzed by Robert Peter,[2] who found that it contained a notable quantity of hydrogen sulphide gas, some carbonic-acid gas, and 440 parts per million of total solids, consisting of sodium chloride and magnesium sulphate, with small traces of iron, calcium and potassium. Reference has already been made to the occurrence of hydrogen sulphide gas in mine drifts at Miami, Okla., and in Kentucky. One of the latter occurrences was in the central Kentucky district and the other in the western Kentucky district. The two waters giving off the gas, as described by A. M. Peter, are very similar. The result of a qualitative analysis of the water from western Kentucky, from a zinc mine 49 feet in depth 4 miles west of Marion and 100 yards from the "White Sulphur Springs" [Crittenden Spring] is as follows:[3]

> Qualitative tests showed the presence of much sodium chloride with some calcium carbonate, calcium sulphate, calcium chloride, a little magnesium chloride, potassium chloride, and lithium chloride. The sediment contained free sulphur, ferrous sulphide, and organic matter.
>
> The presence of free sulphur in the sediment would suggest that the gas which appeared with this water was hydrogen sulphide.

The analysis shows that this is not a surface water but an alkaline-saline carbonated and sulphureted water, similar to the mine water at Miami, Okla., to the deep-well waters of that region, and to the ore solutions which have deposited the ores of the Joplin district. The sediment likewise, in respect to sulphur and iron sulphide, is similar to the reservoir sediments of that district, analyses of which have been given.

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[1] Burk, W. E., The fluorspar mines of western Kentucky and southern Illinois: Min. Industry, vol. 9, p. 294, 1901.

[2] Chem. Rept. Kentucky Geol. Survey, vol. A, pt. 3, p. 152, 1888.

[3] Peter, A. M., Averitt, S. D., and Amoss, H. L., Mineral waters: Kentucky Agr. Exper. Sta. Eighteenth Ann. Rept., for 1905, p. 229 [1906].

In Illinois the igneous rocks are nowhere closely related to the ore bodies, and in Kentucky they are at few places so related. At the Old Jim mine, near Marion, Ky., the ore body extended for a distance of 400 or 500 feet alongside a peridotite dike and for one-third of the distance lay on both sides of the dike. The ore consisted of zinc carbonate and some sulphide, but fluorite was entirely absent. The composition of the ore body was the same at the Lady Farmer mine, on the same dike, a short distance from the Old Jim mine. So far as the evidence afforded by these two deposits is concerned, they may have been formed by cold ascending solutions just as those in the Ozark region or upper Mississippi Valley region were formed, except that here the solutions probably ascended by the same opening as the igneous material. The ascending solutions and the ascending igneous material evidently reached the surface by way of the fissures and the fault planes—the easiest avenues of escape. The ore and gangue minerals could have been transported by cold solutions, but if the solutions were in some places heated through radiation from the dikes they were no doubt rendered more active. Bain and Smith both commented on the absence of dolomite in the gangue and noted the contrast presented in this respect by these deposits to those of the Ozark uplift and of the upper Mississippi Valley, where dolomite is so plentiful. Attention has been called above to the absence of dolomite as a gangue mineral in the veins of central Kentucky and middle Tennessee. Jasperoid is a common gangue in the western Kentucky district, as it is in the Joplin region. The silver content of galena mined in Kentucky is very small, ranging from a trace to 2 or 3 ounces to the ton of concentrates, whereas the silver content of galena mined in southern Illinois has averaged nearly 5.7 ounces to the ton of lead concentrates for the period 1907–1913. A sample of lead concentrates from Rosiclare assayed 9.5 ounces to the ton, according to Whitney,[1] and other reports indicate a range up to 12 or 14 ounces. The lead concentrates of southeastern Missouri average a little over 1 ounce to the ton. Bain lays stress on the presence of antimony in the ores of this district as evidence of their magmatic origin, but, as shown by Williams,[2] a little antimony occurs in the galena of southeastern Missouri, a somewhat larger proportion in the galena of central Missouri, and most of all, amounting to one-half of 1 per cent, in the galena of southwestern Missouri.

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[1] Whitney, J. D., On the upper Mississippi lead region: Wisconsin Geol. Survey, vol. 1, p. 199, 1862.

[2] Williams, C. P., Industrial report on lead, zinc, and iron: Missouri Geol. Survey, pp. 16–17, 1877.

Basing his conclusions on the foregoing statements, the writer believes that most if not all of the ore deposits in western Kentucky have been formed by cold artesian circulating water which was derived from Ordovician formations outcropping in the Cincinnati and Nashville uplifts and which ascended through fissures into the Mississippian rocks, where the ores were precipitated. If some of the deposits in the deep fissure veins, such as those in Illinois that carry argentiferous galena, are due to igneous influences, we have here not a transition type of deposit but a juxtaposition of types—one due to a normal artesian circulation, the other to thermal waters associated with igneous activity.

The occurrence of galena, with little or no sphalerite, in the veins of the Cincinnati and Nashville uplifts and of sphalerite in excess of galena in the western Kentucky region is in line with the place relations of the ores to the intake of the artesian circulation already set forth (p. 212).

OUACHITA UPLIFT.

In Arkansas and Oklahoma the Ouachita uplift, according to Branner,[1] was a low, flat geanticline until after the Pennsylvanian epoch, when it was involved in the Appalachian mountain-making movements and thrown into long, narrow folds. These folds obscure the relation of the ore deposits to the original geanticlinal structure and to the present anticlinorium. At the Kellogg mine, in Pulaski County; the Silver City mine, in Montgomery County; the Cedar Point mine, in Hot Springs County; and the Bellah mine, in Sevier County, Ark., as well as at the place of the recent discoveries on Buffalo Creek in Oklahoma, galena and generally sphalerite, with a little chalcopyrite, occur in veins that cut across the highly folded quartzitic sandstones. The sulphides are generally associated with a gangue of calcite, dolomite, and some barite. These deposits, none of which have developed into paying mines, are, with the exception of those at Silver City, on the north and south sides of the culmination of the Ouachita uplift, to which they bear the same geographic relations as the deposits heretofore described bear to other uplifts. The Silver City deposits are directly upon the uplift.

ARBUCKLE MOUNTAIN UPLIFT.

The Arbuckle Mountain uplift of Oklahoma consists of a core of pre-Cambrian granites and diabases, overlain on the north by the Reagan sandstone, a basal conglomerate formation of Upper Cambrian age; and that in turn is overlain by the dolomitic Arbuckle limestone, in which the ore deposits occur. The Arbuckle limestone is overlain by shales and shaly limestones of Ordovician and Silurian age. The ores consist of zinc carbonate and sulphide in a dolomite gangue. The whole uplift is greatly faulted and, especially in the mining district, is sharply folded. If faulting and folding be disregarded, the general relation of the ore district to the crystalline area is one of a structural slope to the northeast, and it seems reasonable to conceive that an artesian circulation brought up the ores against the inner edge of the shaly members of the overlying formations.

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[1] Branner, J. C., The former extension of the Appalachians across Mississippi, Louisiana, and Texas: Am. Jour. Sci., 4th ser., vol. 4, pp. 357-371, 1897.

LLANO UPLIFT.

The Llano uplift, comprising the pre-Cambrian area of central Texas, is a broad dome surrounded by a scarp of Paleozoic rocks. The geology and mineral resources of the eastern part of the area have been described by Paige,[1] who refers to an occurrence there of lead ore that exhibits such relations to the crystalline rocks and the Paleozoic sedimentary rocks as to suggest its origin from ore solutions having an artesian circulation and notes that the conditions resemble those existing in the disseminated lead region of southeastern Missouri.

DEPOSITS OF LEAD AND ZINC ASSOCIATED WITH THE EASTERN MARGINAL SLOPE OF THE CENTRAL VALLEY.

TENNESSEE.

The ore deposits associated with the geanticlinal uplifts of the central valley of the United States have now been briefly described. It remains to consider any deposits possibly associated with the dip slopes about the eastern margin of the valley. The most promising deposits of this class now being worked are the lead and zinc deposits of eastern Tennessee. These have recently been described by Purdue.[2] They occur in breccias at different horizons in the Knox dolomite, of Cambrian and Ordovician age. This formation, which is underlain by shales and limestones and overlain by Ordovician, Silurian, Devonian, and Carboniferous rocks, occupies a position areally between the Archean rocks of the Great Smoky Mountains and the Pennsylvanian ("Coal Measures") rocks of the Cumberland Plateau—a position analogous to that of the Cambrian and Ordovician of central Missouri and northern Arkansas, with the exception, however, that the rocks in Missouri and Arkansas form a dip slope in which there is an artesian circulation, whereas the rocks between the Great Smoky Mountains and the Cumberland Plateau are thrown into a series of long, parallel folds and overthrust faults, which preclude the possibility of an artesian circulation of any great scope transverse to the folding and faulting. Purdue holds that the ores were originally disseminated through the Knox dolomite and were segregated in the breccias by circulating ground waters but not by surface waters. Hence, deposition probably resulted from ascending waters. The very numerous sink holes indicate active underground circulation and solution. The oxidized ores are naturally more or less residual, as their position shows, but the position of the deposits of the sulphides should give some indication of their relation to the structure. A brief review of the sulphide deposits shows a reasonably close dependence on local structural features. The sphalerite ore bodies northeast of Knoxville, from Love Creek to Mascot, are on a dip slope to the southeast, involving various Cambrian formations, the Knox dolomite (Cambrian and Ordovician), and the Chickamauga limestone (Ordovician). The ores occur in the Knox dolomite within a quarter of a mile of the outcrop of the overlying argillaceous limestone of the Chickamauga formation. The deposits southwest of Leadvale and those near Dandridge have a similar position. The Powell River ore deposits are on the slopes of a broad, gentle anticline in the Knox dolomite.

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[1] Paige, Sidney, Mineral resources of the Llano-Burnet region, Tex., with an account of the pre-Cambrian geology: U. S. Geol. Survey Bull. 450, pp. 75–77, 1911.

[2] Purdue, A. H., The zinc deposits of northeastern Tennessee: Tennessee Geol. Survey Bull. 14, 69 pp., 1912.

VIRGINIA.

The lead and zinc deposits of Virginia are found principally in the Shenandoah limestone, which is the equivalent of the Knox dolomite and of several underlying Cambrian formations as well. The horizon of the ore deposits in Virginia is considerably lower stratigraphically than that of the Tennessee deposits. Lead and zinc deposits in metamorphic schists of probably Cambrian age (according to Watson) in Albemarle County and of pre-Cambrian age in Louisa County will not be considered here. The general structure of the region is similar to that of the eastern Tennessee field, just described, in that it consists of a series of parallel folds and overthrust faults. Watson[1] holds that the metals were originally drawn from the pre-Cambrian rocks and laid down in a disseminated state with the Shenandoah limestone, of Cambrian and Ordovician age, in which formation they have since been concentrated into workable deposits by meteoric waters. The ores form replacement deposits and cavity fillings in breccia and are associated with dolomite and calcite as gangue minerals; in a few deposits a very little fluorspar is found. The ores are believed to have been deposited by the water of an ascending circulation of no very great vertical extent; probably a circulation determined by local structural features, such as have been indicated in discussing the eastern Tennessee deposits. Watson says:[2]

> Recent prospecting about 20 miles west of Austinville, in the extreme southwest corner of Wythe County at Cedar Springs seemingly indicates that the ores occur on or near the faulted crest of an anticline. The distribution, therefore, of the ores in

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[1] Watson, T. L., Lead and zinc deposits of Virginia: Virginia Geol. Survey Bull. 1, pp. 128-133, 1905.

[2] Idem, p. 53.

Wythe County is along a narrow belt which crosses the southern part of the county in a north of east direction. This belt is a structure zone, one of anticlinal folding and faulting, and the ores are deposited along and near the fault in the shattered and recemented limestone of the anticline. Precisely similar relations obtain in the east Tennessee lead and zinc district, which is a continuation southwestward of the Virginia district.

The association of the deposits with anticlinal structural features is good evidence that the ores were deposited by ascending solutions, just as their association with synclinal structures would be evidence in general of descending solutions.

PENNSYLVANIA.

The principal zinc and lead deposits of Pennsylvania are in the Saucon Valley, in Lehigh County, and smaller deposits are at the Bamford mine, in Lancaster County, and at the Sinking Valley mines, in Blair County. The ores are found in fractures, breccias, and cavities in Cambrian and Ordovician limestone, or the "No. II formation" of the Pennsylvania Geological Survey. The unoxidized ores consist of sphalerite and some pyrite. The chief mines in the Saucon Valley were the Ueberroth, Hartmann, and Saucon, which have been well described by Clerc,[1] who attributed the ores to ascending thermal solutions. Lesley[2] opposed this view in the following language:

> The limestone formation in the Saucon Valley lies in a deep trough, into which and to the bottom of which flows the rainfall of the surrounding mountains. The beds are uptilted and broken, the innumerable fissures which traverse them and the caverns which have been excavated in them permit the accumulation of great quantities of water; the dissolution of the lime rocks has produced concentrated masses of zinc ore. * * * Veins of zinc ore do in fact exist in Sinking Valley, opposite Birmingham, but they are concentrations of the zinc and lead from the limestone beds of the valley and there is no good reason for thinking that they are connected in any way with the underground depths. * * * It is evident that the source of the ore was above and not beneath.

Miller,[3] who has recently studied the mines of the Saucon Valley, believes that the iron as well as the zinc deposits were formed by artesian waters. His conclusions are as follows:

> In the formation of the Friedensville zinc deposits it is believed that downward-percolating waters containing carbonic acid derived from the atmosphere and organic matter, sulphuric acid derived from the oxidation of pyrite, and possibly some organic acids dissolved the small disseminated particles of zinc and iron carbonates and sulphides and carried them in solution to places where the water found an easy escape upward, such as occurs in the shattered and faulted zones near Friedensville. Several hundred and perhaps several thousand feet of limestone and shales overlay the present exposed strata, while this work of concentration was most active, and consequently the waters were of considerably higher temperature and had greater soluble power

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[1] Clerc, F. L., The mining and metallurgy of zinc in the United States: U. S. Geol. Survey Mineral Resources, 1882, pp. 361-365, 1883.

[2] Lesley, J. P., Pennsylvania Geol. Survey Summary Final Rept., vol. 1, pp. 436-447, 1892.

[3] Miller, B. L., Economic geology of the Allentown quadrangle, Pa.: U. S. Geol. Survey Bull. (in preparation).

than at present. The abundance of marcasite found with the pyrite indicates, however, that the ore-bearing solutions precipitated their load under moderate temperatures.

The pyrite and sphalerite were deposited in part in the fissures through which the solutions passed and in part as metasomatic replacements of the limestone walls. At the intersections of fissures through which solutions were passing the mingling of waters of somewhat different compositions caused increased precipitation and resulted in the formation of the great masses of ore already described. Metasomatic replacement of the dolomitic limestones seems to have been much more important than precipitation in existing fissures. The dense black finely crystalline masses of sphalerite preserve the texture of the original limestone. In some places the contact between the ore and the limestone is sharp and regular, but in most places it is otherwise, which is explained by the lack of homogeneity of the greater part of the limestone which permitted the solutions to migrate unequal distances from the trunk channels.

The Friedensville ore deposits represent the segregation of zinc minerals obtained from a great thickness of limestones. The limestones in the vicinity of the mines are probably 2,500 to 3,000 feet thick, while perhaps as great a thickness has been removed by erosion. The probability is that the ore was collected throughout a thickness of limestones aggregating 5,000 to 6,000 feet. This is approximately twice the thickness of the limestones of the region, but due to the intense folding to which they were subjected the vertical thickness at any one point was probably doubled.

The process of segregation was undoubtedly slow, but has extended from the close of the Ordovician, when the first great orogenic movements folded and faulted the limestones of the region up to the present. The segregation of pyrite by meteoric waters is still taking place in the region, and no doubt disseminated zinc minerals are likewise being dissolved near the surface, carried downward to great depths, and deposited from ascending waters. Thus the formation of the deposits represents a time interval of millions of years.

The Bamford mine, 5 miles northwest of Lancaster, lies in a synclinal valley of the Cambrian and Ordovician limestones. It contains sphalerite and galena with calcite as a gangue. The Sinking Valley mines are located on the crest of a plunging overturned anticline in the same Cambrian and Ordovician limestone. Their unoxidized ores were sphalerite, galena, and a little pyrite, in a gangue of dolomite with some barite.

Describing the Bamford mine, Frazer[1] quotes E. G. Spilsbury as follows:

> The deposit occurs in the form of two parallel bed veins in the lower Silurian limestones, near their line of contact with the shales of the same epoch, although, so far as developed, the actual line of contact has always been found barren. In this respect the deposit differs from a very similar one in Sinking Valley, Blair County, where the contact lines between the shales and the limestones are quite productive.
>
> The veins at the Bamford mine are most unmistakably bedded veins and not fissures or gash veins. They are conformable both to the stratification and dip of the inclosing rocks. * * *

Lesley[2] concludes as follows:

> All that has been said above proves that these zinc-lead veins are precipitation deposits, are not connected with any deep metallic masses in the underworld, and

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[1] Frazer, Persifor, jr., The geology of Lancaster County: Pennsylvania Second Geol. Survey Rept. CCC, pp. 198-199, 1880.

[2] Lesley, J. P., Pennsylvania Geol. Survey Summary Final Rept., vol. 1, p. 447, 1892.

> can not descend lower than the extreme limit of rain-water percolation in any district of the State to which they belong. * * * I consider them as of the nature of comparative recent cavern and fissure deposits, scarcely at all changed in form by later earth movements.

NEW YORK.

In southeastern New York lead and zinc mines have been worked at Guymard, Wurtsboro, and Ellenville, in Orange, Sullivan, and Ulster counties. The galena and sphalerite, associated with much pyrite and some chalcopyrite, in a quartz gangue, are found in veins in the Shawangunk conglomerate, of Silurian age. These rocks dip steeply westward and are overlain by the shaly Salina formation, also of Silurian age.

Whitney notes the occurrence of lead and zinc in New York as follows:[1]

> Along the southern edge of the great Azoic nucleus of this State, in the counties of Herkimer, Montgomery, and Lewis, many specimens of lead ore have been obtained from the Lower Silurian strata. In the last-named county, near the village of Martinsburgh, according to Prof. Beck, galena is found associated with pyrites, in narrow veins, traversing the Trenton limestone. * * *
>
> Specimens of blende and galena are not unfrequently met with in the Upper Silurian strata, in the neighborhood of Rochester, and from thence to Niagara Falls.

Lead and zinc deposits are known in the Adirondack pre-Cambrian area of northern New York. C. H. Smyth, jr.,[2] describes the famous Rossie lead mines as having been derived from the pre-Cambrian limestone infolded into the granite, comparing the Rossie ore deposits to a lead and zinc vein in Cambrian sandstone overlying the pre-Cambrian limestone near Redwood, where the relations are clearer than at the Rossie mine, 7 miles distant. The Rossie deposits are veins, occupying fissures in the gneiss, and are composed of galena and calcite with subordinate quantities of pyrite, chalcopyrite, and sphalerite.

Smyth says:

> Water circulating through the limestones under pressure and seeking an exit toward the surface would find a ready channel through the crushed zone of the sandstone, depositing during its ascent mineral matter taken up from the limestones. This explanation of the formation of the vein is sufficiently in harmony with all the facts in the case to be regarded with some confidence, and it gives added strength to the hypothesis as applied to the Rossie veins. In both cases it is probable that the vein minerals came from below, and in both cases the crystalline limestone, known to be the carrier of the vein minerals, is present, at Redwood probably directly below the vein, at Rossie in the immediate vicinity and perhaps directly below.[3]

The lead and zinc deposits near Fowler and near Edwards are also found in the pre-Cambrian limestone. The ore body at the Edwards mine lies in limestone dipping 45° NW. and on the hanging wall of a body of talc. Intervening prospects show a fairly definite zone of mineralization having similar relations and extending to the Balmat mine.

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[1] Whitney, J. D., The metallic wealth of the United States, p. 401, Philadelphia, 1854.

[2] Smyth, C. H., jr., The Rossie lead veins: School of Mines Quarterly, vol. 24, pp. 421–429, 1903.

[3] Idem, pp. 427–428.

CANADA.

In Canada galena accompanied by more or less sphalerite is found in numerous veins in the crystalline limestones infolded in the pre-Cambrian rocks. Among the best known mines are the Olden zinc mine, 35 miles north of Kingston, and the Hollandia mine, near Bannockburn, Ontario. The deposit at the Hollandia mine has been described by J. Volney Lewis [1] as occurring in a highly siliceous phyllite or fine-grained quartz schist, which was originally an argillaceous, sandstone. The vein minerals are predominantly galena and calcite which are accompanied by some sphalerite and marcasite. There is no quartz or silicates. The character of the ore and the absence of known igneous rocks in the vicinity of the ore body suggest strongly to Lewis "that both the minerals and the waters by which they were deposited were derived from the adjoining sediments."

The Ramsay lead mine, near Carleton Place, Lanark County, Ontario, is on a galena-calcite vein which cuts the "Calciferous" dolomitic limestone and pinches out in the underlying Potsdam sandstone. The mine is on the southern border of a basin in the Laurentian rocks occupied by Cambrian and Ordovician sediments.

Sphalerite is irregularly disseminated through the Silurian limestone (of Niagaran age) from Niagara Falls northwestward to the head of Lake Ontario. The Albemarle mine is a prospect in this limestone in Albemarle Township, Bruce County, 5 miles northwest of Wiarton. The ore is blende in a calcite gangue.

GENERAL OCCURRENCE OF THE ORES IN BRECCIAS.

The zinc and lead deposits of the Joplin region consist largely of chert breccias having a matrix of jasperoid or dolomite containing sphalerite and galena. Smith,[2] in discussing these deposits, says that the concentration and deposition of the ores were apparently due largely to the brecciation of the rocks, which exposed a large area of rock surface to the action of ore-bearing solution and permitted greater freedom of circulation and consequent greater volume of flow.

The place of contact between a solid and a liquid is the field of operation of the surface energy of a liquid. Ostwald [3] writes of "the phenomenon of adsorption, or surface condensation on solid bodies—that is, the fact that on contact surfaces between solids and liquid solutions the concentration of the dissolved substance is different from and probably always greater than in the rest of the solution." A gas escaping from a solution tends to do so on the face of a solid, the sharp edges of breccias being especially favorable to the liberation of gases from solutions. The influence of breccias in the precipitation of ores may, then, be due to the greater contact surface and the greater number of sharp edges exposed by brecciation, and to adsorption.

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[1] An Ontario lead deposit: Econ. Geology, vol. 1, pp. 682–687, 1906.

[2] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 18, 1907.

[3] Ostwald, Wilhelm, The scientific foundations of analytical chemistry, p. 19, 1900.

The solutions that furnished the ore deposits of the Joplin region are believed to have been ascending alkaline-saline waters containing dissolved carbon dioxide and hydrogen sulphide. As these solutions slowly rose to the surface under artesian pressure they were cooled from, say, 70° F. at a depth of 900 feet to 55° F. at the surface. Further, they were under less and less pressure as they rose, particularly when they reached the "open ground" at the base of the Cherokee shale. These changes favor precipitation of the salts in solution, and the change last noted also favors the liberation of the dissolved gases, which is further favored by the large surface and the sharp edges of the breccia through which the solutions pass. The liberation of the gases, particularly carbon dioxide, results in the precipitation of the metals as sulphides, as already shown. As the solutions undergo these changes, which progressively favor deposition, it may be supposed that, after a solution has ascended to the point where deposition begins, the precipitation will be practically continuous until the portion of the solution at that point has been depleted of metallic salts or has escaped at the surface. Having formed this conception of a continuously precipitating solution rising through the breccias, we may pass to the consideration of the method by which adsorption is especially effective as an aid to precipitation in the breccias.

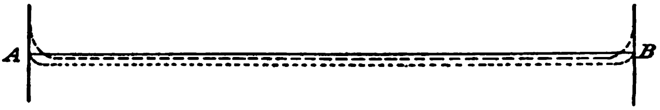

FIGURE 9.—Diagram representing the adsorption concentration curve before and after precipitation in breccias.

The adjacent faces of breccia fragments may be represented by the parallel vertical lines *A* and *B* in figure 9. These vertical lines may be joined together by the horizontal line *A–B*, representing a uniform state of concentration in the solution rising through the breccias—a state of concentration that has just reached the point of saturation for the lead and zinc compounds. According to the laws of adsorption, the concentration of the salts about to be deposited is greater adjacent to the faces of the breccia fragments and increasingly greater in proportion to the fineness of the breccia. The concentration of the solution as regards a metallic salt may be represented, therefore, by the upper broken line—the line of dashes—showing supersaturation adjacent to the wall and something less than saturation in mid-channel. If the solution be conceived as remaining stagnant at this point, deposition should take place upon the solid in the area of supersaturation. As the concentration near the solid is reduced by deposition, the adsorption-concentration curve will be reestablished by movement of the salt from mid-channel to the border and further precipitation will be followed by further redistribution of the concentration, and so on until the concentration at the border is not above the saturation point for the metallic salt and the solution in mid-channel is below the saturation point, represented by the dotted line. This would terminate ore deposition from this solution under these conditions, but, as was pointed out above, the solutions are continually ascending and thus become cooler, are under less pressure, and evolve gases. Therefore, as each portion of the solution is relieved of its supersaturated salt, it makes way for more saturated solution from below and is itself carried farther upward where it again becomes saturated, owing to cooling, relief of pressure, or escape of gases. It is probable, therefore, that once begun the deposition of metallic salts from a solution under the conditions outlined goes on almost continuously until the metals are exhausted or the solution reaches the surface.

Though a descending solution is doubtless subject to adsorption, it does not seem likely that there can be much precipitation from such a solution, as a downward-moving solution is progressively subject to more and more pressure, which increases the capacity of the solution to hold the metals and particularly the gases in solution, and thus opposes the precipitation of ore.

As breccia deposits are characteristic of the ores of the Joplin district, and as such deposits are much more likely to be precipitated from ascending than from descending solutions, they in themselves indicate that the ore was derived from ascending solutions.

CONSTANT INFLOW OF MINE WATER.

Bain [1] believes that a large part of the water that flows into the mines is derived from waters ascending from the Cambrian and Ordovician rocks. His argument in part is as follows:

> The best reason for believing that the ground water is fed mainly from distant sources lies in the fact that the amount of water pumped from the mines is independent of seasonal changes. Except in the case of unprotected openings or very open ground, severe storms and rainy weather do not increase the amount of water that must be handled.

Buckley and Buehler [2] strongly combat this view and assert that very generally in the Joplin district the inflow is 25 to 50 per cent greater in the rainy season than in the dry season. They also maintain that after a mine has been drained very little water comes in from the bottom, so that there is scarcely any inflow of water which may be attributed to an upward circulation.

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[1] Bain, H. F., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 167-168, 1901.

[2] Buckley, E. R., and Buehler, H. A., Geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, p. 21 [1906].

Haworth[1] measured the quantity of water pumped from the mines and the quantity flowing off the tract, and thus obtained estimates of the return flow into the mines and the increment of water from distant sources, the latter amounting to 10 or 15 per cent of the total water pumped. He concludes as follows:

> It would seem that no one could examine the entire territory carefully and observe the vast amount of surface water which reaches the ground through shafts and various kinds of artificial openings, natural "sink holes" particularly, and add to this the much greater amount which must necessarily work its way downward through the soil into the rocks so greatly fissured everywhere in the mining district, without admitting that a large proportion of the water now found in the mining district below permanent water level originates directly from local rainfall. It is equally probable that a portion of this same ground water is migrating westward down the slope of the Ozark area. This migratory water, therefore, comes in part from the catchment areas at or near the summit of the Ozark hills, and in part from additions constantly made to it throughout the entire distance. The eastern catchment area is entirely too small to provide it all.

Reviewing Haworth's report, Bain[2] accepts these results and points out that even if the quantity of water contributed from the deeper horizons be smaller than that of local origin, it is easily possible that it may be the more important in ore deposition.

No doubt the foregoing views are justified by conditions in the Joplin district generally. Special conditions exist in the Miami district, however, and abundant and exact data show that the mine water of that area, which is derived almost entirely from the deeper sources, is remarkably constant in volume at any given level, but that it progressively increases with increase in extent and depth of mining operations. The mines at Miami are entirely beneath the Pennsylvanian shale, the shafts penetrating from 40 to 220 feet of the shale before they reach ore. The collars of the shafts are raised above the reach of surface waters and the clay about the cribbing is well puddled, so that the shafts are practically water-tight, and only a very little surface water reaches the mines, amounting to no more than a shower down the shaft way. One or two cave-ins beneath mill ponds have allowed the ingress of some surface water. In 1908 the writer made a preliminary report[3] on the Miami district, based on examinations made in 1907. His conclusions in regard to the flow of mine water were as follows:

> A circumstance which has delayed the development of the district is that each undertaking requires the raising of 500 to 750 gallons of water per minute. This of

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[1] Haworth, Erasmus, Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, pp. 95–101, 1904.

[2] Bain, H. F., Econ. Geology, vol. 2, pp. 189–190, 1907.

[3] Siebenthal, C. E., Mineral resources of northeastern Oklahoma: U. S. Geol. Survey Bull. 340, p. 102, 1908.

course has been the case in most of the new camps in the Joplin region. With the lowering of the underground water level of mining the amount of pumping ordinarily becomes inconsiderable. In the Miami district, however, the situation is somewhat exceptional. The surface of the ground is low, not more than 25 feet above Tar Creek, the drainage level for the region, and the water-bearing ore stratum is capped by the unbroken Cherokee shale. The mine water is different from the surface water in other camps, being highly charged with H_2S, like the deeper artesian waters, and the height to which it rises may represent artesian head rather than the underground water table. If this be so, there may be no great diminution of the amount of water with time, but on the contrary a possible increase with the development of the underground workings.

R. R. Heap,[1] superintendent of the mines of the Lennan Zinc & Lead Co. and the Miami Zinc & Lead Co. at Miami, has recently published a paper on the drainage problems of the region, in which he gives figures showing the increase of flow within 5 years and from these the following table has been prepared:

Mine water pumped in Miami district, 1907–1914.

Year.	Pumping company.	Depth of mining (feet).	Water pumped (gallons per minute).
1907	New State	90	500+
1908	Queen City-Joplin	126	500
1909	Emma Gordon	163	750
1911	Church-Mabon	230	1,000
1912	Lennan Zinc & Lead	263	1,200–1,250
1913	do	285	1,350
1914[a]	do	[b]320	1,700 } 2,300
1914[a]	Other small pumps		600 }

[a] Communicated by R. R. Heap May 14, 1914.

[b] This depth represents the level of the water at the pump shaft and not the water-table level; the quantity of water raised per minute will therefore gradually diminish until the water table has been lowered to the depth indicated, when a constant flow may be expected of, say, 1,400 or 1,500 gallons at the 320-foot level, which, with the throw of the small pumps, will probably give a total of about 2,000 feet for the camp. This is exclusive of the extreme north mines on Tar Creek and the mines on Horseshoe Lake northwest of Miami.

The first mines opened at Miami were at the south end of the present camp, and in mines opened farther north there was a progressive deepening of the ore horizon in that direction, so that each new mine had to assume the burden of draining the whole camp. The increase in depth and in quantity of water to be pumped is shown in the foregoing table. With each increase in depth of mining it was necessary to lower the water table of the surrounding region to the new depth, and this always resulted in a greatly increased flow of water, which gradually diminished until the new water table was established, when the flow became constant at the figures indicated. Heap[2] has described the pumping operations while lowering the water table from 210 to 263 feet.

> The pump worked almost steadily on a volume of 2,000 gallons per minute for a period of 50 days, when the water level had been lowered sufficiently to permit of

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[1] A geological drainage problem: Eng. and Min. Jour., vol. 96, pp. 1205–1211, 1913.

[2] Idem, pp. 1208–1209.

crosscutting the run. This progressed slowly because of the necessity of closing the door after each round of shots and then waiting for the water to drain below the top valve before opening the lower slide gate, which would let the water drain down sufficiently to swing the door back into the drift safely. The water pouring in from all sides let the H_2S escape, which made it necessary at first to work a double crew half an hour on and off, without even then obtaining good results. These difficulties made the development work progress slowly, and almost two months were required for drifting sufficiently to permit mining a reasonable tonnage.

The first diminution in the inflow was noticeable when the water table receded below the top of the drift door, from which time the decrease continued at the rate of about 100 gallons per minute each week until no seepage through the breccia cementations in the face was noticeable. Since this time, with the face of the drift down dry to the floor, the inflow has remained seemingly constant, being between 1,200 and 1,250 gallons per minute. The total amount of time consumed in the lowering of the water table from the 210-foot level to the 263-foot was five months.

Later data communicated by Heap, under date of April 6, 1914, are as follows:

The volume or inflow of water was the heaviest during the first two weeks in February, there having been a maximum of 2,150 to 2,200 gallons per minute during the second week in February, at which time we had entirely crosscut the run—a width of 120 feet. Since then there has been a gradual diminution, until at this writing we are pumping 1,700 gallons per minute.

As has been noted above, the water table, in May, 1914, had not yet been lowered to 320 feet. Until that point has been reached the quantity of water raised may be expected to diminish slowly until the water table has been lowered to 320 feet, when the flow will probably settle down at 1,400 or 1,500 gallons a minute.

Snider,[1] arguing against an artesian origin for the Oklahoma ores, suggests that "the water in the Peoria and Lincolnville camps is not artesian and that in the Miami camp can probably be accounted for by the rainfall on the territory immediately to the east." The ground-water circulation at Peoria and Lincolnsville is not different from that in other camps of the Joplin region where the Boone formation is the surface rock. The writer has pointed out that the mine waters of the Miami region, when classified according to their geochemical properties, fall alongside the deep-well waters of the region and are not at all similar to the waters of springs and shallow wells. The regularity of flow likewise sets them off from surface waters.

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[1] Snider, L. C., Preliminary report on the lead and zinc of Oklahoma: Oklahoma Geol. Survey Bull. 9, p. 60, 1912.

NONCORROBORATIVE EVIDENCE.

VERTICAL ORDER OF THE SULPHIDES.

VERTICAL ARRANGEMENT OF LEAD, ZINC, AND IRON SULPHIDES IN GENERAL.

The general experience in lead and zinc regions has been repeated in the Joplin district in that lead ores were the principal ores first mined, a preponderance of zinc ores were mined at greater depths, and ores containing more or less iron sulphide were reached in the deeper mines. Many individual ore bodies, however, form exceptions to this general rule. In some mines, especially those associated with carbonaceous shales, which protected the ores from oxidation and solution, pyrite was plentiful near the surface; in others, zinc ores overlay the lead ores. In the sheet ground of the Duenweg-Oronogo belt, which is the deepest level generally mined in the Joplin region, the average ratio of zinc to lead produced in the period 1908–1913 is as 1:0.282, and the average ratio of zinc to lead produced in mines of the open ground of southwestern Missouri for the same period is as 1:0.164, a little more than one-half that mined in the sheet ground, although the open-ground mines are, on the average, not nearly so deep.

It has been contended[1] that this vertical arrangement of the metallic sulphides is prima facie evidence that the solutions depositing the metals were descending, and that the vertical succession merely represents the deposition of the sulphides according to their solubility. So, too, Bain and Van Hise found in this vertical order evidence of the downward sulphide enrichment of the ores.

Since this vertical arrangement of the metallic sulphides is undoubtedly general, so far as ore mined is concerned, it will be well to examine carefully the conclusion drawn therefrom as to the downward flow of the ore solutions and also to indicate certain facts which militate against that conclusion.

VERTICAL ORDER SHOWN BY CHRONOLOGIC RECORD OF MINE OUTPUT OF OPEN-GROUND DEPOSITS.

The order in which the metals have been mined, represented by the statistics of the production of the district, chronologically considered, may be, and in fact is, quite different from the vertical relations of the ores as they were originally deposited and is also quite different from their relations in a single ore body. In other words, because certain ore bodies exhibit these relations and because the order of production of metals has in general exhibited the same succession, it is not therefore safe to argue that all deposits of the region originally showed the same vertical order.

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[1] Buckley, E. R., and Buehler, H. A., The geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, pp. 97–98 [1906].

Buckley and Buehler[1] argue as follows:

> As already explained, we find at Granby, as well as throughout the southwest Missouri district, the major portion of the galena occurring above the blende in heavy beds or chunks at comparatively shallow depths. At Granby this heavy deposit of galena has occurred mainly from 15 to 60 feet beneath the surface, in different parts of the area, although some of the ore has been found at the grass roots. The occurrence of the galena is mainly between flint layers, and is often from 1 to 4 feet in thickness. This method of occurrence precludes the possibility of any mechanical segregation, excepting that due to settling of the entire mass. The galena must have been deposited largely at approximately its present level. These heavy deposits have furnished at least three-fourths of the lead mined in the district, and undoubtedly constitute at least that percentage of the primary deposits. * * *
>
> In the primary deposits by ascending solutions, as shown above, the galena must have been deposited from the neutral solutions in intimate association with the blende throughout the vertical extent of the primary ore body. Considering this massive galena to constitute only three-fourths of the primary deposits, we should have had, in order to have concentrated the lead by a descending circulation, at least three-fourths of the primary ore body extending above the present horizon of the lead. In other words, the present massive segregation of the galena must be near, if not at, or below the base of the first ores deposited by ascending waters.
>
> In order to provide for this vertical distribution of the primary ores, we must conclude that, at the time of their deposition, the Mississippian must have extended stratigraphically, to a considerable height above its present horizon, probably from 100 to 200 feet, and that erosion has carried off this thickness of the Mississippian since the first deposition of the ores.

This argument assumes that the artesian-circulation theory requires that the quantity of lead and zinc sulphides deposited shall be evenly distributed from the bottom to the top of the ore-bearing rocks. This assumption could be true only as it might apply to strictly homogeneous rocks, and even in such rocks we should find the richest deposits near the surface, where the gases escape. In heterogeneous rocks the ores will naturally be deposited in greatest abundance in the strata most favorable to deposition. Other things being equal, the most common deciding factor in favor of deposition, as W. S. T. Smith has pointed out, is the presence of open, brecciated ground. Hence the horizon of great ore deposits in the Joplin district is that zone of the Mississippian which lies just beneath the Pennsylvanian shales and which had developed a karst topography before the shale was laid down. This "open" or "confused" or "soft" ground of the miner has been the great productive zone of the Joplin region. Another horizon at which ores are found abundantly is that known as the "sheet ground" in the Grand Falls chert member of the Boone formation. Other and deeper horizons at which the rocks have yielded some ore and which may become more productive in the future are in the rocks of Kinderhook age and also at the level of the Chattanooga shale.

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[1] Buckley, E. R., and Buehler, H. A., op. cit., pp. 108-109.

The diagrammatic sketch forming figure 10 is the result of an attempt to represent graphically the relation and the vertical distribution of galena and sphalerite in the original deposits before the more or less complete erosion of the Pennsylvanian shale allowed the oxidation, solution, and transfer of the ore in the upper parts of the ore bodies. The figure represents an ideal composite of all the ore bodies of the district and not a section of an individual deposit. The places of greatest lateral expansion of the diagrammatic ore body represent the horizons most favorable to deposition of the ores—that is, the horizons which have yielded the most ore. The diagrammatic ore body has been so drawn as to represent approximately the same relative proportion of lead to zinc as is shown by the total quantity of ore produced in the Joplin district to date. In the absence of any data showing the depth from which the open-ground ores have been derived, or the relative production of mines in the open ground and the sheet ground except during the last few years, it was not possible to make the diagram more than approximately accurate.

A fact generally recognized in the district—namely, that the preponderance of the ores as originally deposited and as recovered by mining were in the uppermost strata of the Mississippian rocks—is shown plainly in the diagram. In the view of the writer the argument of Buckley and Buehler fails to take this fact fully into account, and it also fails to consider fully the differential solution, transportation, and redeposition of the ores. If nothing else remains to show the previous existence of ore minerals at any point in the oxidized zone, their former presence at some places may be inferred from the geologic relations. In some of the mining areas of the Joplin region the country rock is largely limestone and the chief gangue minerals are dolomite and calcite with some secondary limestone. In such areas in the district the ore minerals in the upper part of the deposit might be dissolved and completely transported, leaving absolutely no traces of their former presence. In other areas, however, the country rocks are cherty and the gangue consists largely of jasperoid, a siliceous, resistant rock. Cavities in the jasperoid having the outlines of crystals of galena or sphalerite testify to the

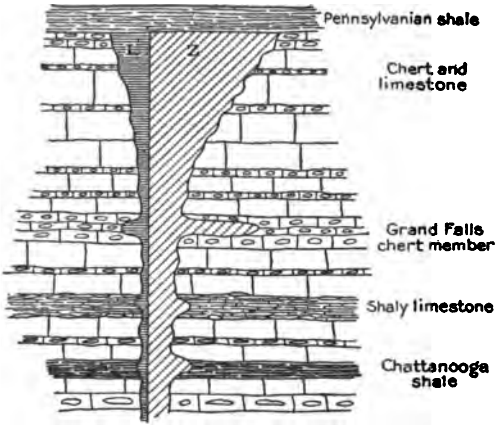

FIGURE 10.—Diagram showing vertical distribution of galena (L) and sphalerite (Z) in the original ore deposits.

former existence of those minerals. Where such cavities in the rocks show that galena has been present, the impressions of the crystals and grains of sphalerite are almost invariably present too. Such impressions of crystals and grains of sphalerite occur also at many places where galena was not present. Hence we may reasonably conclude that the presence of partly oxidized galena in unresistant rocks is generally good evidence of the former presence of sphalerite, though the rocks may now contain no apparent trace of sphalerite. If this conclusion be accepted we may not unreasonably be skeptical of any argument which would attempt to restore the original vertical order of the sulphide deposits from the statistics of production of all ores, sulphide and oxidized.

The metal taken into solution and carried downward may be deposited as the carbonate or as the silicate; or possibly the solution may be carried deep enough to mingle with the deeper ground water, to be changed to bicarbonate, and eventually to be deposited as a sulphide, just as in the original concentration. How deep the solution should go in order to bring about this result can not be determined. As before pointed out, it is quite impossible to say whether the crust of sphalerite deposited on old spikes and like objects in old mine drifts is deposited from normal deeper ground water or from oxidized mine waters. No wurtzite has been seen in such crusts and the inference is that the concentration of acid ions in the depositing solutions was not strong enough to produce that unstable sulphide, which, as Allen[1] has shown, is formed at low temperatures with but small concentration of the stronger acid ions. Allen's conclusions are corroborated by the facts that on the two specimens of sphalerite-incrusted spikes illustrated by Bain[2] there were small calcite crystals, which were undoubtedly formed in place, and that the cementing material was largely calcitic and effervesced freely with dilute acid. It therefore seems probable that sphalerite and galena deposited under such conditions have not been precipitated from strongly acid mine waters but have been derived from solutions not differing greatly from the water of the artesian circulation which originally segregated the ores.

The relations of such transferred metals to the original vertical order of the sulphides may be made clearer by figure 11. The hypothetical original sulphide ore body, outlined by the broken lines, is generalized from the composite ore body shown in figure 10 (p. 231), by omission of the irregularities which represent the heavier deposits at the more favorable horizons. This ore body, expanding laterally to indicate the heavier deposits in the "open ground," terminates upward against the Pennsylvanian shale. That part of the former galena (*a*) above the present surface is represented as having been carried downward, either residually or in solution, and is now found at (*b*), adjacent to the primary galena ore. The galena, both original and transported, is shown as extending to the present surface of the land, for some galena is even now found at the "grass roots." The transported lead is either residual galena or cerusite or redeposited galena or cerusite. Similarly the space (*c*), indicating the area leached of ore on the zinc side of the hypothetical ore body, includes not only the area of the former sphalerite ore body above the present land surface but also a very considerable area below it, showing the greater solubility of zinc ores as compared to lead ores. The zinc leached from (*c*) has been carried downward to the region (*d*), and there deposited as carbonate, silicate, or sulphide. The foregoing statement as well as the diagram expresses the truth in general terms, of course. It does not mean that the ore dissolved from the upper part of any particular ore body is necessarily deposited against the lower part of that same ore body. On the contrary, the ore removed may be added to some distant deposit; and the ore body from the upper part of which it was removed may have received similar additions from afar.

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[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 34, pp. 355–360, 1912.

[2] Bain, H. F., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 158–159, 1901.

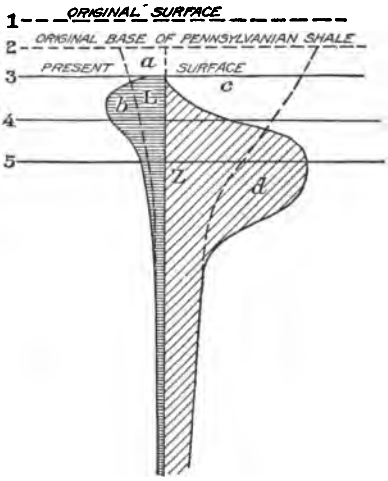

FIGURE 11.—Diagrammatic reworked ore body showing vertical distribution of galena (L) and sphalerite (Z) after erosion and solution of upper deposits.

It is evident that if we take the ratio of zinc to lead at several equidistant levels, such as lines 3, 4, and 5 in the diagram, we shall get a constantly increasing figure as we go downward until we pass the zone of maximum secondary[1] deposition, below which we should find that the ratio of zinc decreases until we reach the bottom of the zone of secondary deposition, where the ratio of galena to sphalerite is that which is normal to the primary sulphide deposits of the district. As the horizon of the sheet ground is largely if not altogether below the zone of secondary deposition, the ratio of galena to sphalerite in the deposits at that horizon should be greater than in the deposits higher up in the column, except in strata near the surface, where the zinc has been in large part leached away.

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[1] The terms "primary" and "secondary" as used above have a somewhat wider significance than as ordinarily used in discussions of downward sulphide enrichment. The new ores may be carbonates or silicates as well as sulphides; the ores are not necessarily and perhaps not even commonly added to the lower part of the same ore body from which they were extracted; the secondary sulphide ores are not deposited as such by substitution for another sulphide; and finally, enrichment is not a necessary consequence of the solution and redeposition of the metals. So used, the terms mean simply original and derived. So far as may be seen the derived or secondary sulphides do not differ from the primary sulphides, and in fact the only thing that can be definitely determined is that some of the sulphides are of a later generation than the others.

The diagram assumes that about half of the total lead in the reworked ore body lies above line 4, which is approximately 50 feet from the present surface. Therefore, according to the diagram this 50 per cent of the total lead has been derived from 50 feet of formation plus approximately 40 feet of eroded formation below the shale. Buckley and Buehler[1] say that at least three-fourths of the lead mined in the Granby district has been derived from within 60 feet of the surface, and they give 74,000 tons of galena ore as the production of Newton County prior to 1894, and 11,000 tons of galena as the production of the Granby district from 1894 to 1904, inclusive. However, if we take the lead production of the whole of Newton County since 1893, the lead production before 1894 is not so preponderant. According to figures which the writer has compiled from Winslow's reports and from the reports of the Missouri Bureau of Mines and Mine Inspection, the lead content of ores mined in Newton County up to and including 1893 was approximately 54,100 tons and the lead content of ores mined from 1894 to 1913, inclusive, was 33,888 tons. In other words, about 60 per cent of the total production of lead to date was mined before 1894. Winslow's[2] report, published in 1894, gives the depths at that time of various mines in the Granby district as about 50 or 60 feet. Therefore 60 per cent of the total lead production to date came from within 50 or 60 feet of the surface. If we bear in mind that the lead production year by year will go toward reducing the preponderance of lead mined before 1894, we can see that the figures quoted above to show the lead production of Newton County are in complete harmony with the proportions of the diagrammatic reworked ore body. Furthermore, it must be apparent that the validity of the artesian-circulation theory does not, as maintained by Buckley and Buehler, depend on the assumption that as three-fourths of the total lead so far mined has come from the upper 50 or 60 feet of the Mississippian limestone, the formation of the total deposit of lead ore must have involved the erosion of about 200 feet of similar beds that overlay the existing beds. This assumption is not at all necessary, for, owing to the expansion of the ore bodies in the "open ground" at the base of the Pennsylvanian shale, the differential transfer of the zinc which has occurred must have been amply sufficient to furnish the preponderance of lead found at the upper level.

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[1] Buckley, E. R., and Buehler, H. A., The geology of the Granby area: Missouri Bur. Geology and Mines, vol. 4, 2d ser., p. 109 [1906].

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 602-606, 1894.

VERTICAL ORDER OF GALENA AND SPHALERITE IN CAVITIES IN THE SHEET GROUND.

In the typical sheet ground of the Oronogo-Duenweg belt the ore occurs in sheets between ledges of chert, and these sheets represent original strata of limestone that have been replaced by siliceous jasperoid in which the sulphides of lead and zinc are disseminated. There may be 8 to 12 or more of the ore sheets separated by the barren chert ledges, the whole making up an ore face 8 to 12 feet high. Owing to irregularities in the chert ledges many cavities were left between the upper surface of the jasperoid and the overlying chert. Most of these cavities have been partly or wholly filled with ore. The crystals of galena and sphalerite have an etched appearance, but it is generally impossible to determine whether this appearance is the result of solution or is simply the form assumed by the crystals. Where there is evidence of later generations of the sulphides the amount of sulphides deposited is inconsiderable. Hence to all appearances the ores are the product of original or primary deposition. In a cavity containing both galena and sphalerite the galena is in the upper part and the sphalerite in the lower part. Figure 12 shows in a general way the conditions that exist in the cavities of the sheet ground. The crosshatched layers are jasperoid containing disseminated sphalerite and galena. The strata between are chert, in which the jointing shown is purely conventional and does not signify that there is really any jointing within the limits of the sketch. In the cavities the galena clings to the roof and the sphalerite fills the lower portion of the space.

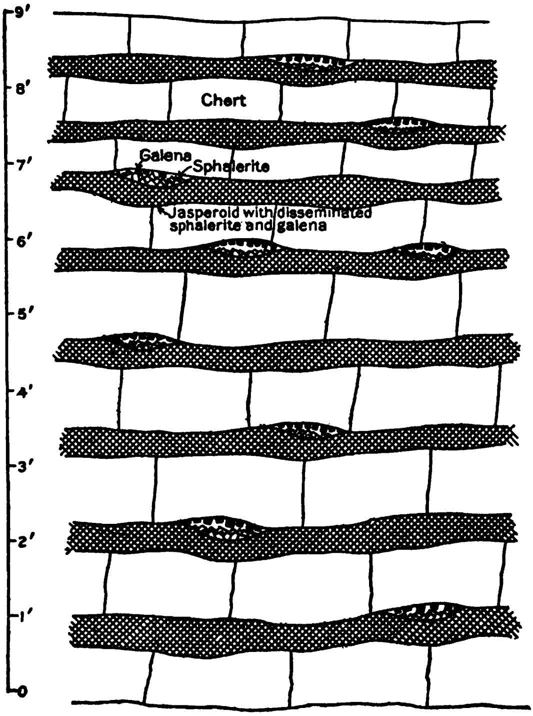

FIGURE 12.—Sketch illustrating the occurrence of "pockets" or cavities in the sheet ground and the relation of galena and sphalerite in the cavities.

Figure 13 is from a sketch, drawn to scale, of a cavity in the sheet ground at the Underwriters' Land Co.'s "Yellow Dog" mine. This cavity (see fig. 13) is more or less exceptional in that the roof is flat instead of being concave upward. A mass of galena, conforming to the shape of the pocket, clings to the roof. Jasperoid with disseminated sphalerite fills the lower portion of the pocket and its disposition, it being thinner on the bottom and thicker at the sides, shows that it can not have solidified from a mud, as some have supposed, for the mud would undoubtedly have been thickest over the lowest place in the bottom. The jasperoid has apparently replaced a sheet of limestone. In the bottom of the cavity, resting upon the jasperoid, is a thin sheet of sphalerite crystals; over this is a half-inch sheet of sphalerite with a little jasperoid; and the remainder of the pocket is filled with sphalerite.

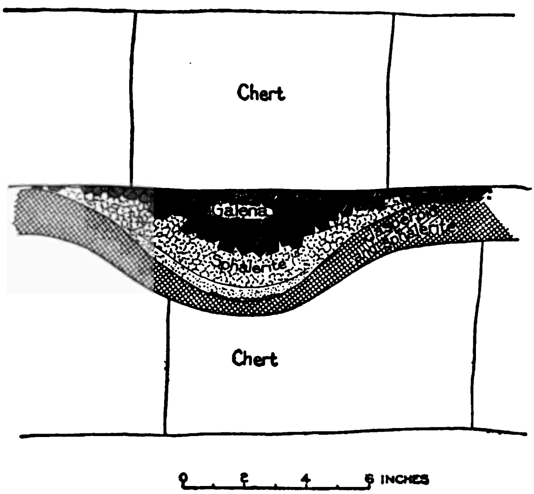

FIGURE 13.—Section of a cavity in sheet ground at the Underwriters' Land Co.'s Yellow Dog mine, Webb City, Mo.

This arrangement of galena and sphalerite in the cavities has been interpreted as a manifestation of the vertical order of sulphide deposition and hence as evidence that the ore solutions were descending. Several facts, however, militate against such an interpretation:

1. If the solutions descended into empty cavities the sulphides should be more or less stalactitic in form, and should consist of galena in the upper part and sphalerite in the lower, or of galena in the central core with sphalerite surrounding it. But, whether stalactitic in form or not, we should certainly expect the sphalerite to be attached to the galena. As a matter of fact the galena clinging to the roof of the cavity occurs in large, well-developed cubes and the sphalerite on the bottom of the cavity is of the usual habit of that found in cavities, there being generally a horizontal opening between the galena and the sphalerite. It is plain that the first galena formed in the cavities was deposited on the roofs of the cavities and that the first sphalerite formed was deposited on their bottoms.

2. If the solution carrying the metals descended or ascended into such a cavity already filled with the solution, we should expect the metals in solution to be diffused through the stagnant solution in

the cavity. Under such conditions there is no apparent reason to be drawn from the differential solubilities of the sulphides why the lead sulphide should seek the roof of the cavity and the zinc sulphide should seek the bottom of the cavity.

3. The galena and sphalerite in many of these deposits are surmounted, or even incrusted, with marcasite. If the sulphides have been deposited in vertical order from descending solutions all the marcasite in the cavity should be found in the lower part, associated with the sphalerite.

4. As there are eight to twelve or more sheets of ore in the ore face of the sheet ground, a number of cavities may lie nearly in a vertical line, and in all the cavities the galena has been deposited above the sphalerite, a fact that is difficult to explain if the ores were deposited from descending solutions in the usual vertical order.

5. As the chert strata are unbroken and practically impervious over considerable areas beneath which jasperoid has replaced limestone, it is reasonable to suppose that the solutions have here moved laterally for considerable distances. If this supposition is true (and facts at hand seem to substantiate it), then the occurrence of galena above sphalerite in cavities in these areas, instead of being evidence of descending solutions, is a phenomenon itself requiring explanation.

It has already been pointed out that the ratio of lead to zinc in the sheet ground is about twice what it is in the open ground above, a ratio altogether unlike what we should expect to find if the sulphides were deposited in the usual vertical order from descending solutions.

VERTICAL ORDER OF GALENA AND SPHALERITE IN CAVITIES IN THE OPEN GROUND.

In the open, broken ground deposits many flat slabs of chert or limestone are apparently surrounded by gangue material carrying disseminated ore. The gangue may consist altogether of jasperoid containing disseminated ore, or it may consist of calcite, dolomite, or secondary limestone, or of all three together, carrying disseminated ore. It is evident that such slabs, exclusive of the supporting bases, have been surrounded by the ore solution. Even if the solution were descending it would necessarily have to flow around the slab to reach its under surface. Yet at a great many places the vertical habit of occurrence of galena and sphalerite in cavities has asserted itself under such slabs, the galena clinging to the under surface of the slab and the sphalerite occurring some distance below, the two being separated by gangue material. Figure 14 represents an example from the Argosy mine at Spring City. Figure 15 represents an interesting illustration of the same habit in the Halloween mine, at Spring City. The peculiar structure here shown is found also in some replacements by dolomite, and is probably inherited from the original limestone.

Figure 16, representing the manner of occurrence of the ores in the Ruby Trust mine, at Granby, Mo., is copied from Buckley and Buehler.[1]

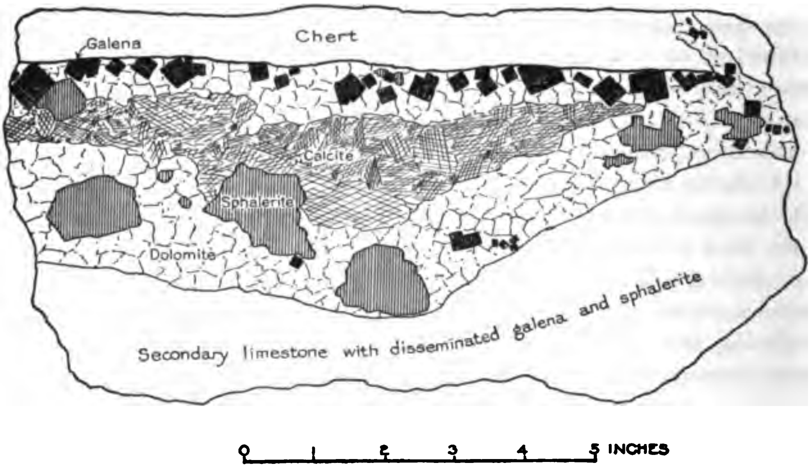

FIGURE 14.—Galena over sphalerite in cavity in the Argosy mine, Spring City, Mo.

ORE BODIES IN BRECCIA-FILLED CAVITIES.

Smith[2] believes that the observed vertical order of the sulphides represents normal deposition from ascending solutions, and cites in proof the distribution of the sulphides in the Hegoda mine, of Joplin. The ore body in this mine was of elliptical outline, measuring 90 by 140 feet, and reached a depth of 70 feet. The ore was first mined from the top and ore was taken out progressively downward to the bottom of the deposit. The record of the output of the mine thus represents in fair measure the vertical order of occurrence of the sulphides from the top downward. At first galena was in excess, then galena and sphalerite were about equal, then sphalerite was

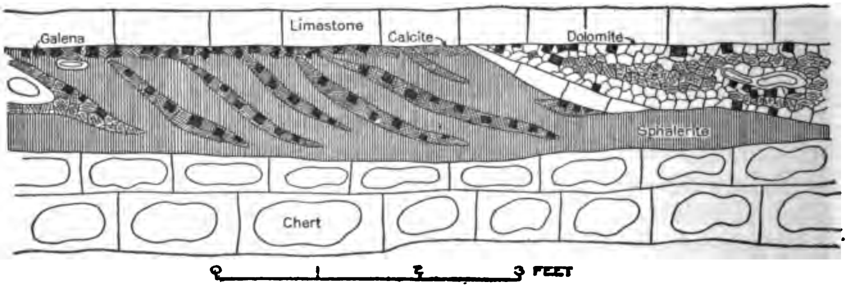

FIGURE 15.—Galena over sphalerite in the Halloween mine, Spring City, Mo.

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[1] Buckley, E. R., and Buehler, H. A., Geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, p. 60 [1906].

[2] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 17, 1907.

much in excess, then galena was in excess, and finally, at the close of operations, galena and sphalerite were nearly equal but the ore carried considerable pyrite. This circular ore body was in chert accompanied by more or less dolomite, and was overlain by a patch of Pennsylvanian shale and of the same shape and size in horizontal cross section as the ore body. Oxidation had scarcely more than begun, as indicated by softened dolomite, tallow clay, and mud at the top of the ore body, but there were no signs that any of the sulphides had been dissolved and carried lower. Smith thinks there is little doubt that the ore was the result of primary concentration by ascending waters, and therefore concludes that the vertical relations of the sulphides shown by the ore body were dependent on conditions governing the deposition of the ores from ascending solutions. He intimates that the explanation of the vertical relations of the sulphides in ore bodies may be akin to the explanation of their relations in cavities in the sheet ground, relations such as have already been described, which he suggests may be due to the preference exhibited by galena and sphalerite, as well as by calcite and dolomite, for certain of the bounding walls of the cavities in which they occur.

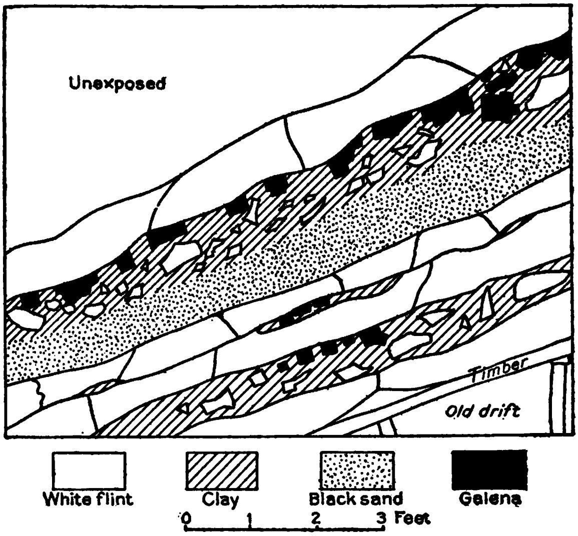

FIGURE 16.—Manner of occurrence of the ores in the Ruby Trust mine, Granby, Mo., after Buckley and Buehler. "The galena is attached to the roof, and the calamine forms a sheet parallel to the cap rock."

The ore bodies in the open ground occur in coarse breccias in which there must be the greatest degree of freedom of circulation. Such an ore body is, in effect, a deposit in a breccia-filled cavity, in which the conditions controlling ore deposition must be essentially similar to those holding in small cavities.

VERTICAL ORDER OF ORE BODIES BENEATH THE PENNSYLVANIAN SHALE.

At Miami, Okla., the surface covering of Pennsylvanian shale has prevented surface water from reaching the ore bodies and hence there has been no oxidation and solution of the deposits and no formation of oxidized ores or secondary sulphides. The Pennsylvanian shale must also have prevented the descent of surface solutions during the deposition of the ores. Nevertheless, the galena tends strongly to occur in the upper parts of the ore bodies and to take the upper surface of small cavities, whereas the sphalerite tends to take the lower parts. This arrangement can not possibly be explained as a manifestation of the vertical order of sulphide deposition by downward-moving solutions, because no solutions moved downward in this area. The arrangement of the sulphides in this region, therefore, must be normal to or imposed upon the deposition from ascending solutions.

LATERAL ORDER OF SULPHIDES IN SHEET GROUND NEAR THE "CORNFIELD BAR."

Those who see in the ore deposits of the Joplin region a vertical order of sulphide deposition representing the relative solubilities of the sulphides have in mind, unconsciously perhaps, the deposition of the sulphides by descending solutions in a confined fissure or vein in which there is not sufficient precipitant to bring down all the metals. If there is an excess of precipitant in such a fissure all the sulphides will naturally come down together. There is nothing strictly comparable to a vein or fissure in the Joplin region, yet very generally in the sheet ground and at many places in the open ground, especially where the ores occupy an underground water channel, the flow of the solutions, which was there lateral instead of vertical, was to a considerable extent confined. In such places galena might appear in greater force near the source of supply—that is, the master opening—sphalerite coming in stronger as the distance from the master opening increases. In most such places the excess of precipitant in the solutions might, by throwing down all the sulphides, obliterate any trace of a lateral succession in the deposition of the sulphides, depending on the direction of flow. Nevertheless a tendency toward such a succession has been observed. Several years ago the writer described[1] a structural feature in the sheet ground which he called the "Cornfield bar," a long narrow belt of open, bowldery, shale ground which reached from the surface downward through the ore-bearing sheet ground that stretched away on either side. Manifestly this opening, with either ascending or descending solutions, was the master opening and was the chief path taken by the solutions. Ascending under pressure or descending under gravity or by diffusion the solutions would naturally spread out in the sheet ground. It was a matter of common observation among the operators of the sheet-ground mines adjoining the "bar" that the ratio of galena to sphalerite was greater near the bar than it was farther away. Evidently the solutions moving out into the sheet ground exhibited a tendency to deposit the sulphides in the reverse order of their solubility. Yet it was in this very area, while studying the "Cornfield bar," that the writer first had opportunity to note the universal superposition of galena on sphalerite in pockets in the sheet ground. If the lateral order just described was due to lateral currents, then the vertical order in the pockets was due to something entirely disconnected from the direction of flow of the solutions.

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[1] Siebenthal, C. E., Structural features of the Joplin district: Econ. Geology, vol. 1, pp. 119-128, 1905.

DIFFUSION A GREATER FACTOR THAN DIRECTION OF FLOW.

As the ore solutions in the openings in the sheet ground and in the cavities of the open ground must have moved very slowly, or have been practically stagnant, diffusion must have been almost everywhere sufficient to overcome any tendency toward deposition of the sulphides in a vertical order dependent on the flow of the solution. Only such physical forces as come into play in a free cavity filled with a mixed solution can have operated. Buckley and Buehler have commented on the effect of diffusion as follows:[1]

> Diffusion becomes of the utmost importance in slowly moving waters, as below the level of ground water. It is thought that the location of the major portion of the secondary galena in the upper part of the openings, where it is associated with the calamine, is largely due to this factor.

The present writer is at a loss to understand how diffusion accomplishes the concentration of the galena in the upper part of the openings and why the effectiveness of diffusion should be limited to solutions depositing secondary galena. It would seem that any slow-moving or stagnant ore-bearing solution should be subject to diffusion, and if there be some inherent property of lead requiring it to seek the upper bounding surface of the cavity for a locus of deposition that property should be as effective with lead in primary solutions as in secondary solutions.

ATTEMPT TO REPRODUCE THE VERTICAL ORDER EXPERIMENTALLY IN A QUIESCENT SOLUTION.

In an attempt to reproduce in the Survey chemical laboratory the conditions of such segregation, Chase Palmer put a mixture of lead and zinc solutions in a glass cylinder, in the center of which a bar of clean iron was suspended vertically. A feathery, dark precipitate formed on the iron bar and arranged itself in two nodes, the middle of the bar being nearly free. The precipitate was very light and fell away from the iron bar when it was removed from the solution, so that no quantitative determinations could be made. W. George Waring, of Webb City, Mo., repeated the experiment at my request, using a bar of aluminum and dividing the solution midway of the bar with a membranous septum. The precipitate, which formed mostly during the first few hours, was analyzed with these results:

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[1] Buckley, E. R., and Buehler, H. A., Geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, pp. 98-99 [1906].

Analyses of precipitates of lead and zinc formed on a bar of aluminum.

[W. George Waring, analyst.]

	Milligrams.
On upper part of bar:	
Lead	310.8
Zinc	11.9
Sulphur	4.8
On lower part of bar:	
Lead	302.3
Zinc	14.0
Sulphur	4.5

The precipitates thus consist almost wholly of metallic lead and are but a form of the familiar "lead tree." Although the precipitates on the upper and the lower parts of the bar do not differ materially, the slight difference shown indicates the deposition of more lead above and more zinc below. If precipitation could be made somewhat slower, with more nearly equal precipitation of zinc and lead, especially if they were thrown down as sulphides, possibly the vertical differentiation obtained experimentally might more closely approach that found in nature.

CONCLUSION.

The vertical order of deposition of galena and sphalerite manifests itself beneath impervious slabs, where the solutions must have moved horizontally. It shows itself in deposits beneath a covering of impervious shale, where there can have been no descending solutions. That the ratio of lead to zinc in the ore mined in a district decreases as mining progresses from the upper levels to the lower levels is not proof of an original vertical order but is a result of the reworking of the ore bodies induced by the differential solubilities of the sulphides, together with the deposition lower down of the metals leached from the ore bodies. With a sufficient supply of the precipitant there can be no order of deposition, for all sulphides come down together. The vertical arrangement of the sulphides, as found in the Joplin region, is therefore apparently independent of the direction of flow of the solutions.

The writer inclines to hold that the vertical relations exhibited by galena and sphalerite when they arrange themselves in a cavity, whether a small cavity, as in the sheet ground, or a large cavernous opening filled with breccia, as in the open ground, is a molecular phenomenon, a manifestation of the inherent molecular activities of these two minerals. The two sulphides seem in some way to be able mutually to orient or polarize each other in a vertical direction. It is quite within the bounds of possibility that radial earth currents may be concerned in the phenomenon.

SYNTHESIS OF IRON AND ZINC SULPHIDES.

The work of E. T. Allen[1] and his associates at the Geophysical Laboratory of the Carnegie Institution has thrown much light on the relations to each other of the two disulphides of iron—pyrite and marcasite—and on the like relations of the two sulphides of zinc—sphalerite and wurtzite. It has shown that pyrite and sphalerite are the stable forms, marcasite and wurtzite inverting to pyrite and sphalerite, respectively, at temperatures of about 450° C.[2] and about 1,020° C. The temperature 450° C. is not definitely fixed, but at a temperature as low as 400° C. no change could be observed during the time of a laboratory experiment. The change at 450° C. is not reversible like that which occurs at a true "inversion point," but it goes in only one direction and becomes slower and slower as the temperature falls until at low temperatures it is infinitesimal or zero.[2] At different temperatures, constant from four to six weeks, crystallized pyrite, marcasite, sphalerite, and wurtzite were obtained. Crystalline marcasite has been repeatedly made at room temperature and pure pyrite has been prepared at 70° C. Sphalerite has not been crystallized below 200° C., and wurtzite not below 250° C.[2] From alkaline solutions only the stable compounds, pyrite and sphalerite, were formed; from acid solutions marcasite and wurtzite were obtained, and sometimes pyrite and sphalerite. The following rules were found to hold: (1) At a given temperature the greater the acid concentration the greater the quantity of marcasite or wurtzite formed; (2) with a given acid concentration the higher the temperature the greater the quantity of pyrite or sphalerite formed; (3) the lower the temperature the lower the acid concentration required to yield a given quantity of marcasite or wurtzite. Although the authors specifically warn the reader that the interval between the temperatures at which the crystallized sulphides were obtained and the temperatures of normal ground water is too great to be bridged by extrapolation, yet it seems necessary to consider the general trend of the results in relation to the problem of ore deposition in hand, particularly as the microscopic examination (see pp. 186–187) of the sediments from the springs at Sulphur Springs, Ark., showed only pyrite depositing from those waters which are faintly alkaline or neutral.

The sulphides of the Joplin district here considered are pyrite, marcasite, and sphalerite. Wurtzite has been found in small crystals in a single mine. (See p. 258.) According to the results expressed above, marcasite is deposited from acid solutions only, at temperatures as low as 25° C., and both pyrite and marcasite may be deposited from such solutions at temperatures between 70° and 300° C. It is but natural to see reason in this for believing that the Joplin ores must have been deposited from acid solutions at temperatures normal for ground water. Yet there are difficulties in the way of sweeping conclusions. For instance, there is the association of marcasite and calcareous rocks. Allen says:[1]

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[1] Allen, E. T., Crenshaw, J. L., and Johnson, J., The mineral sulphides of iron, with crystallographic study by E. S. Larsen: Am. Jour. Sci., 4th ser., vol. 33, pp. 169–236, 1912.

Allen, E. T., and Crenshaw J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 34, pp. 341–396, 1912.

[2] Communication from E. T. Allen, July 17, 1913.

> There is one fact concerning the occurrence of marcasite and metacinnabar which should be mentioned. Both are sometimes associated with calcite. Whether or not they are paragenetic is a doubtful question. (Lindgren.) If the calcite is not subsequent to the sulphides one would be led to suspect that the original solution must have contained bicarbonates and sulphates. The synthetic work would lead us to expect pyrite from such a solution; still the quantity of free acid required for pure marcasite is very small at low temperatures and it may be that the reaction $FeSO_4+H_2S+S=FeS_2+H_2SO_4$ would produce marcasite when the initial concentration of acid was no greater than it is in calcium bicarbonate solutions.

The common association of marcasite with calcareous rocks has been remarked by Julien,[2] who, contrasting marcasite with pyrrhotite, says:

> This [marcasite] is a steely grayish white mineral, often affected by a greenish tinge, crystallizing after an entirely different system, the rhombohedric, and having a peculiar tendency to originate in calcareous rocks, e. g., the chalk of England and the Carboniferous and Trenton limestones of this country. From a pound of the latter rocks from Jefferson County, N. Y., digested in acid, over an ounce of marcasite, in drusy crusts of pure and brilliant crystals, was left as a dark sediment.

And further:[3]

> Marcasite constitutes largely or altogether the pyrites occupying thin seams or coatings in the coal beds, lignitic shales, and dolomites of Saxony and Cornwall, the chalk, many limestones of America, and, in general, the unaltered sedimentary rocks, such as sandstones, graywacke schists, peat, clay, bituminous coals, casts of fossils, and also veins of galenite.
>
> The common occurrence of this mineral in calcareous beds, e. g., the chalk of England, the Trenton limestone of New York, the Carboniferous limestones of Wisconsin and Illinois, etc., suggests the possibility that the presence of calcium carbonate, under certain conditions, may determine the crystallization of iron disulphide as marcasite rather than pyrite in a way similar to that of the crystallization of calcium carbonate as aragonite rather than calcite in the presence of strontium carbonate gypsum, or salts of lead, as shown by Credner.

The interior of many of the large scalenohedral crystals of calcite that line Roach's Crystal Cave, in the outskirts of Joplin, Mo., contain zones of slender rods or fibers of marcasite, which are arranged normal to certain planes that probably represent crystal faces, though such planes rarely coincide with any faces on the crystals.[1] A calcareous geode from central Missouri that is lined with small calcite scalenohedrons contains rhombic dodecahedrons of pyrite, which are penetrated by blades of marcasite, and both the pyrite and the marcasite are imposed upon or partly or wholly embedded in the calcite crystals. Blades and rods of marcasite penetrate the calcite crystals in all directions. There can be no possible doubt that the marcasite and the calcite are paragenetic. Furthermore, in the Joplin district calcite and dolomite are among the common gangue minerals. Dolomite, with sphalerite and galena, is disseminated through jasperoid, showing that their deposition is contemporaneous.

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[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 34, p. 382, 1912.

[2] Julien, A. A., The microscopical structure of the iron pyrites: N. Y. Microscopical Soc. Jour., author's separate, p. 3, 1886.

[3] Julien, A. A., On the variation of decomposition in the iron pyrites, its cause and its relation to density: New York Acad. Sci. Annals, vol. 3, pp. 395–396, 1886.

Meteoric waters containing carbonic acid enter the underground circulation, and in passing through rocks containing calcium or magnesium carbonate a portion of the carbonic acid combines with the calcium or magnesium carbonate, taking it into solution as the bicarbonate, in this wise:

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$

If the rocks are sufficiently calcareous to use up all the carbonic acid in the water in forming calcium bicarbonate, nearly all this will hydrolyze, giving an alkaline reaction to the water, thus:

$$\begin{array}{rll} Ca(HCO_3)_2 + 2H_2O = & Ca(OH)_2 + & 2H_2CO_3 \\ & Ca'' & 2H \\ & 2OH' & 2HCO_3 \\ & \text{Complete.} & \text{Very slight.} \end{array}$$

The ionization of calcium hydroxide is nearly complete, but that of carbonic acid is slight, so the concentration of hydroxyl ions is greater than the concentration of hydrogen ions and the reaction is alkaline.

But if a considerable excess of carbonic acid remains in solution, by ionization as above, the hydrogen ions may equal the hydroxyl ions in concentration, making the water neutral in reaction; or the hydrogen ions may exceed the hydroxyl ions in concentration, and then the water becomes acid in reaction.

Both the shallower and the deeper waters of the Joplin region carry free carbon dioxide, and as the deeper waters contain less of the earthy bicarbonates in solution they are likely to contain a larger proportion of free carbon dioxide, though this statement is scarcely susceptible of proof by the analyses herein given, for the quantity of free carbon dioxide in any water can be determined accurately only at the well or spring, and such determinations are not usually made. Both the shallow and the deep waters are therefore probably slightly acid in the chemical sense of that term. (See pp. 85–88.)

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[1] This interesting occurrence of marcasite rods in calcite crystals has been described at some length by H. E. Merwin (Am. Jour. Sci., 4th ser., vol. 38, pp. 355-359, 1914). It had also been briefly noted by Arthur Winslow (Missouri Geol. Survey, vol. 7, pp. 566-597, 1894) and by A. F. Rogers (Kansas Univ. Geol. Survey, vol. 8, p. 477, 1904).

However, the term "acid water," as used in connection with mines and ore deposits generally, indicates a water containing free radicles of the stronger acids—such as sulphuric, hydrochloric, or nitric—and as the acid mine waters are usually a result of the oxidation of sulphide ore bodies, the predominating acid radicle is usually sulphate. As already noted (p. 196), it is acid waters of this character that Buckley and Buehler had in mind in discussing the origin of the Joplin deposits. The occurrence of ores with calcite and dolomitic gangues would seem to negative the conception of free strong acids in the solutions from which they were deposited. Wurtzite, as is pointed out above, has been obtained only from solutions containing free strong acids. Noelting,[1] who has made perhaps the most extensive study of wurtzite, reached the conclusion that wurtzite is always secondary. If secondary it must have been deposited from acid solutions. Wurtzite occurs in the United States in quantity at the Gagnon mine at Butte, Mont.,[2] and in the Horn Silver mine, near Frisco, Utah,[3] and it is believed to be secondary at both places and to have been deposited from descending acid sulphate solutions. A little wurtzite also occurs at Goldfield, Nev., as noted by Ransome,[4] and in the Era district, Idaho, as noted by Umpleby.[5] The occurrence at Goldfield is thought to be due to deposition from descending sulphate waters, but the deposit in Idaho is intergrown with calcite in such a way that Merwin[6] and Allen[7] conclude that the wurtzite and calcite have crystallized simultaneously out of solutions that were practically neutral, or at least that contained no acid stronger than carbonic acid. The small crystals of wurtzite reported from the Joplin district (see p. 258) may have been deposited from nearly neutral waters containing free carbonic acid, such as water of the artesian circulation, but the rarity of the mineral and its occurrence, so far as known, only in stalactites (see pp. 258–264) has led the writer to conclude that in the Joplin district it is secondary in origin, having been deposited from descending acid sulphate waters. However, the practical absence of wurtzite in the Joplin deposits points to the practical absence of waters containing the strong acids and indicates the deposition of the ores from solutions no more acid than calcium carbonate solutions. We find demonstrably recent deposition of blende upon iron implements in mines and upon the walls of abandoned and submerged mine drifts, but no example of the deposition of wurtzite.

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[1] Noelting, Johannes, Ueber das Verhältniss der sogenannten Schalenblende zur regulären Blende und zum hexagonalen Wurtzit: Inaug.-Diss., p. 28, Kiel, 1887.

[2] Pearce, Richard, The association of minerals in the Gagnon mine, Butte City, Mont.: Am. Inst. Min. Eng. Trans., vol. 16, pp. 62–64, 1888.

[3] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, pp. 93–95, 149–150, 1913.

[4] Ransome, F. L., Wurtzite at Goldfield, Nev.: Washington Acad. Sci. Jour., vol. 4, pp. 482–485, 1914.

[5] Umpleby, J. B., Geology and ore deposits of the Mackey region, Idaho: U. S. Geol. Survey Prof. Paper in preparation.

[6] Merwin, H. E., The simultaneous crystallization of calcite and certain sulphides of iron, copper, and zinc; a crystallographic study: Am. Jour. Sci., 4th ser., vol. 38, p. 357, 1914.

[7] Allen, E. T., and Crenshaw, J. L., Effect of temperature and acidity in the formation of marcasite (FeS_2) and wurtzite (ZnS); a contribution to the genesis of unstable forms; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 38, p. 429, 1914.

Therefore, so far as the synthetic experiments by Allen and his associates throw light on the subject, they indicate that the Joplin ores were deposited from solutions of no greater acidity than calcium bicarbonate solutions. Under the artesian-circulation theory the ore solutions are identical with the water of the bordering deep wells, which carry calcium and magnesium bicarbonate in solution as well as free carbon dioxide and hydrogen sulphide.

The sediments from White Sulphur Spring and Black Sulphur Spring at Sulphur Springs, Ark., contain zinc, lead, copper, and iron, according to the analyses cited in the table on page 164. These waters, when examined by Allen, were found to be neutral or faintly alkaline. Under the microscope (see pp. 186–187) the sediments showed pyrite crystals but no marcasite, sphalerite, or galena. Calcite crystals are forming with pyrite in the White Sulphur Spring and quartz crystals are forming with pyrite and impure calcite in the Black Sulphur Spring. Waring's analysis of White Sulphur Spring (No. 35 in the table) shows 6.1 parts per million of free carbon dioxide. The odor of hydrogen sulphide is plainly discernible about both springs, and Menke's analysis of "sulphur" water (No. 72 in the table), taken probably from the Black Sulphur Spring, showed that the water held a small quantity of the gas in solution. Marcasite forms contemporaneously with calcite (see pp. 244–245), but here calcite and pyrite are forming, with no marcasite. The ore solutions therefore appear to have belonged in the neutral zone in which a slight increase in the amount of carbonic acid could change the character sufficiently to determine the formation of marcasite but not enough to permit the formation of wurtzite.

QUANTITATIVE TESTS OF THE ARTESIAN-CIRCULATION THEORY.

SUFFICIENCY OF SOURCE.

The average thickness of the Cambrian and Ordovician rocks of the Ozark region as originally deposited must have been not far from 1,500 feet. In this series of rocks there are four or more sandstone formations, having a total thickness of about 350 feet. Robertson's analyses, already cited (p. 78), show the zinc content of the dolomitic limestones in the series, but the sandstones were not tested for their metal content. They may therefore be omitted from any estimate of the total zinc content of the Cambrian and Ordovician rocks, so that the thickness of dolomitic limestones to be considered is 1,150 feet. A square mile of sediments 1,150 feet thick would have a volume of 32,060,160,000 cubic feet. The area of the Ozark dome lying within the margin of the Pennsylvanian rocks, and therefore subject to the artesian circulation, is about 40,000 square miles. Buckley and Buehler [1] give the weight per cubic foot of seven samples of dolomitic limestones of this series, taken from several quarries in Missouri. The average weight for the seven samples is 156.1 pounds per cubic foot. Robertson's analyses show that the Cambrian and Ordovician limestones contain an average of 0.0425 per cent of zinc. By taking the total volume per square mile in cubic feet, the total area in square miles, the weight per cubic foot, and the average zinc content as factors we find that these limestones contain 42,539,000,000 tons of zinc.

The total zinc content of ore produced in the Ozark region to 1912, inclusive, as near as can be figured is about 3,250,000 tons. We may allow as much more for future mining. The loss of zinc in mining and concentrating in the Ozark region is about 50 per cent, so that the total original zinc content of ore bodies mined and to be mined in the region was 13,000,000 tons. The quantity of zinc in deposits that will never be discovered and in deposits too lean to work is hard to estimate, but we may put it at 26,000,000 tons, equal to twice that in deposits which have been mined and in deposits which will be mined, making a total of 39,000,000 tons of zinc, which we may accept as a reasonable estimate of the zinc that has been leached from the Cambrian and Ordovician rocks, transported down the dome, and segregated into workable or unworkable ore bodies.

By comparing this 39,000,000 tons with the 42,539,000,000 tons of zinc which, according to Robertson's analyses, the Cambrian and Ordovician rocks originally contained, it is seen that less than one one-thousandth of their zinc content has been leached from those rocks.

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[1] Buckley, E. R., and Buehler, H. A., The quarrying industry of Missouri: Missouri Bur. Geology and Mines, 2d ser., vol. 11, pp. 88, 95, 96, 98, and 102, 1904.

After due allowance has been made for the fact that, as Robertson's samples were collected largely from the central and eastern parts of the uplift and were therefore laid down nearer to the original Archean nucleus they were possibly richer in the metals than the average rock of the region, it is nevertheless plain that the Cambrian and Ordovician rocks were an ample source of the zinc.

SUFFICIENCY OF TIME FOR ORE SEGREGATION.

As the average thickness of the Cambrian and Ordovician rocks of the Ozark region as originally deposited must have been not far from 1,500 feet, a square mile of these rocks 1,500 feet thick would contain 41,817,600,000 cubic feet. Buckley and Buehler[1] give the porosity of seven samples of dolomitic limestone of Cambrian and Ordovician age taken from various quarries in Missouri. The average for the seven samples is 9.5 per cent. At this average porosity the total pore space in a square mile of dolomitic limestone 1,500 feet thick would be 3,972,772,000 cubic feet. The pore water filling this space at 62½ pounds to the cubic foot would weigh somewhat more than 124,000,000 tons.

Chase Palmer determined the zinc content of the water of a deep well at Claremore, Okla., as 0.75 of a part per million, and of the water of the waterworks well at Pittsburg, Kans., as 0.44 of a part per million; and E. H. S. Bailey determined the zinc content of the Pittsburg water as 0.6 of a part per million. The average of these three determinations is 0.6 of a part per million. W. George Waring has determined the zinc content of the water from the Whitaker Park well at Pryor Creek, Okla., as 1.5 parts per million. It is possible that these waters are richer in zinc than the average, but on the other hand it is very probable that the first water circulating through the rocks dissolved and carried away more of the metals than were carried by the waters in more recent time. The average figure, 0.6 of a part per million, may therefore be regarded as a moderate estimate of the average zinc content of the ground water in the Cambrian and Ordovician formations from which the Claremore and Pittsburg wells draw their supply. The pore water in 1 square mile of these sediments, 1,500 feet thick, would therefore contain, in round numbers, 75 tons of zinc. As already noted, the area of the Ozark dome within the margin of the Pennsylvanian is about 40,000 square miles. This would give a zinc content of 3,000,000 tons in the pore water of the Cambrian and Ordovician formations of the Ozark region. It has already been estimated that 39,000,000 tons of zinc has been leached from the rocks and transported to the present deposits. If the pore water contains 3,000,000 tons of zinc, it will need to be changed 13 times to transport 39,000,000 tons.

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[1] Buckley, E. R., and Buehler, H. A., The quarrying industry of Missouri: Missouri Bur. Geology and Mines, 2d ser., vol. 2, pp. 88, 95, 96, 98, and 102, 1904.

The average radius of the Ozark dome inside the Pennsylvanian border is about 120 miles. The average radial path of water flowing down the sides of the dome will therefore be about 35 miles; but the mean effective artesian path will be longer than this, for the belt of shallow circulation (largely in Mississippian rocks) near the margin of the dome should not be included in estimating the mean, though its width should be added to the mean when that is derived. If we estimate this belt as about 25 miles in width, we shall have about 60 miles as the true effective mean artesian path, and this is probably not far from right. Now, if the water has to flow down the sides of the dome and be replaced 13 times, the total time necessary will be the time required for water to travel 13 times 60 miles, or 780 miles.

In the absence of experimental data it is difficult to make an estimate of the rate of flow through such rocks. The pore spaces in dolomitic limestone are probably in large part discontinuous, so that the rate of flow would be slow. But it is not at all necessary or even reasonable to assume that the radial flow down the dome is through the dolomite itself. A large part of the water undoubtedly flows through joints, through arenaceous or otherwise porous strata, and along the bedding planes. This assumption, however, does not imply that such flow will not be effective in dissolving the metals from the dolomite and transporting them to the mineral areas. To the writer it seems more likely that the searching out and solution of the disseminated metals in the limestones is the work of ground water that saturates the limestones and works its way downward or upward (downward in the earlier and upward in the later stages of its artesian journey) through the dolomitic strata from one bedding plane or porous layer to another. Such passage would be relatively short and would deliver the metals to the more swiftly moving solutions in trunk channels by which they would be transported to the areas of mineralization. The rate of flow to be estimated, then, is that in the trunk channels and aquifers of the Cambrian and Ordovician rocks of the dome.

The main aquifer of the Cambrian and Ordovician of the Ozark area is the St. Peter sandstone, or "Pacific" sandstone, as it has been known in Missouri. This sandstone varies in size of grain from fine to coarse. No measurements of the porosity or grain of this sandstone from Missouri are known, but Buckley[1] gives the porosity of St. Peter sandstone from Argyle, Wis., as 19.06 per cent and gives a microphotograph of a thin section from which the average diameter of the grains can be calculated at about 0.27 millimeter. The average slope of the Ozark dome from the center toward the southwest is figured at 6.6 feet per mile. By substituting these data in Slichter's formula[1] for calculating the flow through soils, we get a probable rate of flow through the St. Peter sandstone of 6.8 feet a year. To insure an estimate that will not be excessive, 5 feet a year will be taken, and no estimate will be made of the flow through joints and along bedding planes. In order to change the ground water 13 times, the number of times necessary to transport the total quantity of zinc contained in the ore bodies 780 miles, as computed above, it would require somewhat more than 800,000 years.

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[1] Buckley, E. R., On the building and ornamental stones of Wisconsin: Wisconsin Geol. and Nat. Hist. Survey Bull. 4, p. 252, and pl. 66, fig. 2, 1898.

This estimate is based on the assumption that the area affected by the circulation was always as large as it now is. As a matter of fact, however, the area was at first small, and has gradually grown to its present size. The average radial distance the water has flowed during the period of its circulation is therefore but one-half the average distance it would have flowed had the area been constantly of the present size. For this reason it will be necessary to double the estimate reached above, and this will give us the minimum period for the transportation of the ores. As 1,600,000 years is but a short period compared with the lapse of time since the post-Carboniferous elevation which gave the Ozark uplift the outline of its modern structure and established the artesian circulation and began the segregation of the ores, it would seem that this test shows that there has been ample time for the segregation of the ores in the manner postulated by the artesian-circulation theory.

DILUTION OF CONNATE WATER.

Let us now consider the effects of the dilution of the alkali metals and the chlorine of the connate water, or original sea water inclosed in the sediments when they were laid down. If the original pore water had the composition of sea water, then by the time an equal quantity of fresh water had entered the artesian circulation the mineral content of the original pore water would have been diluted to a certain extent, say one-half.

The problem is rather complicated and, for the sake of illustration, we may take first the case of simple dilution. If we add an equivalent volume of fresh water to the sea water and pour off half, we have diluted the saline constituents of the remaining portion to one-half. If we again add an equivalent volume of fresh water and pour off half we have diluted the original saline constituents to one-fourth; in other words, the dilution increases in geometric ratio. With 13 dilutions, that is, 13 changes of water, the number which we have seen would be necessary to segregate the ores of the uplift, we shall have diluted the original salines to $\frac{1}{8192}$ of their original strength. But the effect of adding ground water to a saturated formation in its receiving area as fast as that formation gives up ground water in its discharging area is more complicated. If into one end of a U tube filled with a quantity of saline solution an equivalent quantity of water is poured, saline solution of practically full strength will be discharged at the other end and the remaining solution in the tube will be diluted much more than one-half. The larger the cross section of the tube in proportion to the volume added and the less the velocity of flow, the more chance for mixing the solution and for diffusion and therefore the less the resulting dilution, which, however, can not be less than one-half. In small twisting passages, such as pore spaces, the flow is extremely slow, there is great opportunity for diffusion, and, moreover, the salts in solution are adsorbed by the walls of the passages; so that in fact the dilution of the saline elements in the renewal of ground water may approach the minimum (one-half) indicated above. This possibility is further strengthened by the following consideration. The water that replaces the connate water will not be pure but, as it was originally meteoric and had flowed through dolomitic limestones, it will carry a relatively high content of the alkaline earths and sulphates and a low content of alkali metals and chlorine. Connate sea water diluted by such a water will therefore not be depleted of its alkali metals and chlorine to the same degree as if it were diluted by pure water and it will gain in its content of alkaline earths and sulphates. The principal constituents of sea water, according to Dittmar,[1] are given in the first column of the following table; the second column shows the saline constituents of sea water divided by 8192, representing the dilution by 13 changes of water; the third column gives for comparison the average saline constitution of 13 deep-well waters in the vicinity of Joplin, Mo., all the well waters for which good analyses are available.

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[1] Slichter, C. S., Theoretical investigation of the motion of ground waters: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, p. 322, 1899.

Saline constituents of sea water and of water of deep wells near Joplin, Mo.

[Parts per million.]

Constituent.	Sea water.	Sea water divided by 8192.	Average of 13 deep wells in Joplin district.	Excess of column 3 over column 2.
Alkali metals (Na, K, etc.)	11,104	1.4	12.0	9×
Alkaline-earth metals (Ca, Mg, etc.)	1,736	.2	60.5	290×
Chlorine (Cl)	19,390	2.4	7.2	3×
Sulphate (SO_4)	2,696	.3	14.4	44×

Assuming that the figures in column 3 represent the salinity of a sea water which has been diluted 13 times, we find, by comparing these with the figures in column 2, that while each of the metallic bases and acids is present in greater quantity than the simple dilution would call for, the excesses are just what would be expected when the character of the diluting solution is taken into account. The greatest excess is naturally to be expected in the alkaline earths and the next largest in sulphate, for reasons already given. Since the diluting solution, as already remarked, was necessarily not altogether free from the alkali metals or chloride, it follows that excesses in those substances also are possible. Nevertheless, when it is borne in mind that the constituents of the sea water have been divided by 8192, it seems to the writer that if the average alkali content of the deep-well waters of the Joplin region is only 9 times the hypothetical alkali content and the average chlorine content is only 3 times the hypothetical chlorine content, these facts indicate strongly that the actual dilution of the connate saline pore water was of the order here indicated.

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[1] Murray, John, and Hjort, Johan, The depths of the ocean, p. 176, London, 1912.

There are several possibilities to be considered in this connection. The connate water may have represented a sea of different salinity from the present ocean. The Cambrian and Ordovician strata may have contained saliferous deposits which furnished salt to the artesian circulating water and thus helped to conserve its salinity. Lastly, no account has been taken of the dilution that came about during late Mississippian and early Pennsylvanian time, when the Mississippian limestone land was exposed to erosion and carved into a karst topography over much of the uplift. As has been already pointed out under the heading "Stratigraphy" (p. 26), the Mississippian rocks probably completely covered the Ozark dome at that time and hence may have effectually protected the underlying Cambrian and Ordovician rocks from the ingress of surface waters.

With these things in mind, it seems to the writer that the calculated number of changes of ground water necessary to transport the zinc agrees so closely with the apparent dilution of the connate sea water that it constitutes presumptive evidence of the identity of the processes and is a fair quantitative test of the artesian theory.

ENRICHMENT.

EXTENT OF ENRICHMENT IN THE JOPLIN DISTRICT.

Much difference of opinion has existed as to the extent of enrichment, more particularly of downward sulphide enrichment, in the Joplin region. Jenney recognized secondary deposits of blende, galena, chalcopyrite, greenockite, marcasite, and pyrite produced by alteration of the primary sulphides in the zone of oxidation and reduced to sulphides by organic matter lower down, but he evidently regarded them as of minor importance. Winslow derived the deposits from the overlying and adjacent rocks by lateral secretion and downward flow, but recognized no addition of sulphides derived from the oxidation of the upper parts of the ore bodies themselves. Bain, on account of the vertical arrangement of the ores, thought that the greater number of the ore bodies were formed by downward sulphide enrichment, though he admitted that deposits formed by ascending solutions might show the same vertical arrangement. Buckley and Buehler, for the same reason, held that the sulphide ore bodies were formed by downward-moving solutions and that there has been little, if any, enrichment of the sulphides. Haworth concluded that oft-repeated enrichment from surface erosion of the ore bodies has been the main agency in the accumulation of the ore bodies. W. S. T. Smith minimized the importance of downward sulphide enrichment and concluded that the vertical order observed was due to ascending solutions. All agree upon the difficulty of distinguishing the secondary sulphides from the primary sulphides. There are no pseudomorphs of galena after sphalerite or of galena and sphalerite after marcasite or pyrite. The only evidence that there has been replacement of any sulphide by another sulphide is seen in the films of greenockite, galena, and covellite to be described later. Most of the writers mentioned above have contended that the ore metals were carried mainly as the sulphate and were precipitated as the sulphide by organic matter or hydrogen sulphide. If both ascending and descending solutions were of the same character, met the same precipitants, and deposited the sulphides in the same cavities without replacement, there is apparently no way to distinguish the later from the earlier generations of the sulphides. It has been suggested that the occasional small ruby-red crystals of sphalerite are secondary, but of this there is no good proof. The color is due partly to the size of the crystal, for in the same hand specimen the thinner translucent edges of the larger crystals of sphalerite of regular appearance may be just as ruby-red as the smaller crystals.

The crusts of sulphide ores deposited on old spikes, rails, and bits of iron in abandoned and submerged mine drifts, as illustrated by Bain,[1] may at first thought seem to have been formed by secondary sulphide deposition from descending solutions, but they are not certainly so, for when an old drift in the Joplin region fills with water and the underground water table is raised some distance above the drift, one can not say what portion of the water in the drift is derived from the artesian circulating water. Moreover, the fact that these deposits are formed on iron has no significance, except to show that the sulphides are recent. Any ore metal reduced from solution through the influence of metallic iron would be precipitated in the metallic state, as is shown by the "lead tree" precipitate described on another page. Most of the crystals of galena and sphalerite on the spikes are separated from the metallic iron by a layer of iron oxide. In some of the objects so incrusted it is difficult to determine whether the ore minerals are not accidental aggregates cemented by iron oxide, but in the two examples illustrated by Bain (the originals of which are at hand) there can be no doubt that the ore minerals crystallized in place, as the crystals are small and of perfect form, not cleavage fragments, such as would occur in any accidental aggregate. The sulphides were not deposited in acid sulphate waters, however, for on one of the specimens there are several small scalenohedral crystals of calcite, which evidently crystallized in place. Moreover, the cement of the aggregated crystals in both specimens is largely calcium carbonate and effervesces freely with dilute acid.

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[1] Bain, H. F., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 158–159, 1901.

RESIDUAL ENRICHMENT.

Enrichment through residual concentration has doubtless occurred at many places. Such concentration has generally involved galena, which is not so soluble as sphalerite, but at some places cerusite, smithsonite, and calamine also have been concentrated through the solution and removal of limestone gangue, leaving the ore minerals embedded in yellow clay and chert bowlders. Most of the very rich shallow deposits that were worked in the early days of mining in the district were doubtless formed by such residual concentration.

OXIDE ENRICHMENT.

Bain used the term "oxide enrichment" to include that addition to the ore bodies which results from the precipitation as carbonates or silicates of the metals taken into solution in the upper oxidizing zone. Such precipitation would usually be a result of reaction with the wall rock or with substances held in solution in the ground water. Alteration of the ore minerals in place would not, of course, result in enrichment. The formation of smithsonite by replacement of limestone and of calamine by replacement of jasperoid has been fully described by Smith.[1] However, both calamine and smithsonite at times have been deposited directly from solution without reaction with any solid substance, as is shown by the globular crystal aggregates of those minerals, which at places surmount the sulphide minerals. No doubt both oxide enrichment and residual enrichment have contributed to the formation of the rich shallow "silicate" deposits.

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 19, 1907.

SULPHIDE ENRICHMENT.

PROCESSES INVOLVED.

Downward sulphide enrichment includes the removal in solution of ore minerals from the upper part of an ore body and their precipitation as sulphides in the lower part of the same ore body. The process of sulphide enrichment has been very fully discussed by Emmons.[1] Thought of as taking place in a single ore body within definite walls, the concept is simple; thought of as taking place in the complex ore bodies of the open, broken, confused ground of the Joplin region, however, the concept becomes complicated. The present ore bodies of the Joplin region undoubtedly incorporate some metals which, in their journey down the dome, have taken part in the composition and decomposition of ore bodies many times. Owing to the direction of the underground circulation of the dome, those constituents of an ore body that are taken into solution in the zone of oxidation will be carried downward and very likely also to some extent laterally, so that they may be added to another part of the same ore body, or to some other ore body, or they may be disseminated through rocks at a distance from any ore body. It therefore follows that only a portion, possibly a small portion, of the metals taken into solution from any ore body will be redeposited in that same ore body. This is true of oxide enrichment, but seems especially true of downward sulphide enrichment, because the dissolved metal must almost invariably descend into the deeper circulation to reach an available precipitant. Movement downward to this extent will likely be accompanied by considerable lateral movement, carrying the metals farther away from the immediate ore body from which they were derived. For these reasons it is believed that downward sulphide enrichment has been of very minor importance in the Joplin region.

There are several forms of sulphide deposits in the Joplin region which with fair safety can be said to be sulphide enrichments; among these are greenockite films, galena films, covellite films, wurtzite crystals, and stalactitic blende.

GREENOCKITE FILMS.

The blende from the Joplin district carries a small percentage of cadmium, as the writer[2] has elsewhere noted. Nine composite analyses of about 45,000 samples, mostly carload lots shipped between 1900 and 1913, show the average cadmium content of Joplin blende to be a little more than 0.3 per cent, equal to $\frac{1}{186}$ of the zinc content. Of course this cadmium may not all be isomorphously mixed with the blende, but may in part represent the secondary greenockite described below as due to downward sulphide enrichment.

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[1] Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, 1913.

[2] Siebenthal, C. E., Cadmium: U. S. Geol. Survey Mineral Resources, 1908, pt. 1, pp. 795-796, 1909.

Jenney[1] noted that greenockite is a secondary mineral in the deeper levels, derived by alteration of cadmiferous blende in the zone of oxidation and precipitated below by the reducing action of organic matter. Smith,[2] following Waring, also cited the occurrence of powdery films of greenockite upon sphalerite or other minerals as an example of downward sulphide enrichment. Smith says:

> Greenockite is not uncommon near the lower limit of the zone of weathering, where it occurs as a product of secondary enrichment. It is most abundant on the surface of sphalerite crystals or on fracture surfaces within them, but is also found on galena, calcite, chert, and calamine. As a coating it forms very thin dull films, easily rubbed off with the finger and with a color ranging from grass-green through yellowish green to citron-yellow.

Some of the coatings, however, adhere firmly, and when they are removed leave the surface of the blende much tarnished, possibly etched, indicating replacement of the blende. Apparently the cadmium sulphide is formed sometimes by replacement and at other times by precipitation through reducing agents already in solution, as, for instance, when deposited as easily removable powders, or when deposited on calcite and other minerals not sulphides. Rogers[3] points out that some of the yellow films contain no cadmium and that the yellow coating on some calcite crystals is zinc sulphide instead of greenockite, concluding that "it is not sufficient to call every yellow coating greenockite."

However, greenockite does occur, and most of it must be secondary, since where it occurs there has always been oxidation and solution of the upper part of the deposit; but in the Miami district, where the surface formation, Cherokee shale, has prevented the oxidation of the upper part of the ore bodies, there is no greenockite.

Even if zinc to the amount of 186 times the cadmium in the greenockite films had been carried down and secondarily deposited, the total quantity would be of minor economic importance.

GALENA FILMS.

According to W. S. T. Smith, galena is occasionally found in dull, very dark gray or blackish films on the surface of sphalerite, or in lustrous films, with the characteristic color of galena, coating cleavage surfaces of sphalerite and penetrating some distance into its interior. These films tested chemically give good reactions for lead sulphide. They are always found close to the lower margin of the zone of oxidation, having been formed in the process of sulphide enrichment.

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[1] Jenney, W. P., The lead and zinc deposits of the Mississippi Valley: Am. Inst. Min. Eng. Trans., vol. 22, p. 199, 1894.

[2] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 19, 1907.

[3] Rogers, A. F., Minerals of the Galena-Joplin district: Kansas Univ. Geol. Survey, vol. 8, pp. 460-461, 1904.

COVELLITE FILMS.

Rogers[1] describes similar films of covellite as follows:

> Sphalerite from the Big Coon mine on West Seventh Street in Galena is often coated with a bluish-black substance which penetrates the cleavage surfaces for a considerable distance, or, perhaps, as often, is entirely replaced by it in the form of a soft material of submetallic luster of the same color. This mineral has been identified as covellite. We therefore have covellite pseudomorphous after sphalerite. It seems probable that a metathetic reaction has taken place between the zinc sulphide and copper sulphate, thus: $ZnS+CuSO_4=CuS+ZnSO_4$. Such a reaction does take place when sphalerite is heated in a closed tube containing a solution of copper sulphate to a temperature of 200° C., as experiments by the author show. Given sufficient time and favorable conditions, may not this reaction have taken place without the high temperature? Associated with the covellite and exterior to it is malachite, which is probably a further product of the decomposition of the covellite.
>
> Galena from Cooper Hollow, Galena, is often partially replaced by cerusite, the unaltered galena remaining as a corroded fragment in the cavity. In these cavities covellite is found as an earthy, bluish-black material. Perhaps here the reaction $PbS+CuSO_4=CuS+PbSO_4$ has taken place.
>
> An average of two analyses of the pseudomorphs from the Big Coon mine by Mr. Edgar B. Hayes gave the results in column 1. Calculating the Fe as FeS, Zn as ZnS, representing the unchanged sphalerite, and deducting this and the SiO_2 and recalculating to 100 per cent, we have the figures in column 2, while the theoretical [composition] for covellite is given in column 3.

Composition of covellite.

	1	2	3
SiO_2	4.47		
Cu	18.80	67.10	66.40
Fe	1.17		
Zn	43.68		
S	31.37	32.90	33.60
	99.49	100.00	100.00

WURTZITE CRYSTALS AND STALACTITIC SPHALERITE.

Wurtzite is known from one locality in the Joplin region. Rogers,[2] who was the first to describe wurtzite from the district, gives the locality as an abandoned mine at the north end of the Missouri Lead & Zinc Co.'s land east of Joplin. The mineral is described as occurring as small hemimorphic hexagonal pyramids, with dull luster, averaging about 2 millimeters in length and 1 millimeter in thickness. These crystals are generally attached at the apex, the other end being terminated by a basal plane. The wurtzite crystals are either implanted on the sphalerite or occur in openings or cavities in it. The massive zinc sulphide upon which the wurtzite crystals are implanted has a botryoidal, mammillary, or stalactitic form. Rogers believes that this massive zinc sulphide is also wurtzite, because of the close association of the wurtzite crystals with it, because of the similarity of color, streak, and powder, and, lastly, because some particles of the powder of the massive mineral seem to be doubly refracting. The massive zinc sulphide shows peculiar reticulate intergrowths of galena.

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[1] Rogers, A. F., Minerals of the Galena-Joplin district: Kansas Univ. Geol. Survey, vol. 8, pp. 459–460, 1904.

[2] Rogers, A. F., Annotated list of minerals occurring in the Joplin lead and zinc district: Kansas Univ. Quart., vol. 9, p. 163, 1900; Minerals of the Galena-Joplin district: Kansas Univ. Geol. Survey, vol. 8, pp. 461–462, 1904.

Smith[1] has described such intergrowths as follows:

> Intricate skeleton intergrowths in stalactitic form of fine-grained galena and fine-grained radial sphalerite are common at the Combination mine, east of Joplin, forming what is called "combination ore," impossible to mill satisfactorily. * * * Galena constitutes the central part of the stalactitic forms, branching out in skeleton growths intermixed with fine-grained radial sphalerite which forms the outer and main part of most of the stalactites. More or less marcasite sometimes coats the outside of these galena-sphalerite stalactites, and stalactites were also noted formed chiefly of marcasite with a small central core of granular galena.

Chamberlin[2] has described and illustrated similar reticulated galena from Wisconsin as follows:

> These reticulated forms also occur in the center of stalactitic aggregations of galena and blende, the reticulated cavities taking the place of the central cylindrical opening, common to stalactites. * * *
>
> There is a form, likewise styled reticulated galena, that seems to owe its origin in part to the primal mode of its crystallization. It appears to have grown up along an extended octahedral axis by accretions to the adjacent faces, the result being an elongated prism capped by a pyramid. After this elongated crystal had attained certain very moderate dimensions, and apparently while it was yet growing, there sprang out thickly along its length a series of lateral crystals that grew in a similar manner, but at right angles. These are imbedded in blende and seem to have grown simultaneously with it, and to have been modified by their struggles with the competitive mineral, resulting in mutual encroachments, which produced, in the galenite crystals, successive contractions and enlargements of an irregular and unsymmetrical sort. Subsequently the interior seems to have been, in part, redissolved after the manner above indicated, mainly along the central axes, but also on the margins and in irregular ways. The total result is that, being imbedded in blende and dependent on its irregular fracture for exposure, most specimens present a very complicated aspect. Its theoretical interest lies mainly in the fact that it is one of the evidences of the strictly contemporaneous deposition of lead and zinc ores.

The Combination mine referred to by Smith is on the land of the Missouri Lead & Zinc Co. and is doubtless the mine from which came the specimens described by Rogers. The writer obtained some material of the same sort from Ward's Natural Science Establishment, Rochester, N. Y. The only locality given is Joplin, but there can be little doubt that this material likewise came from the Combination mine.

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 12, 1907.

[2] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geology of Wisconsin, vol. 4, pp. 385-386, 1882.

This material has stalactitic, botryoidal, and massive forms of sphalerite, each of which shows the skeletal intergrowths of galena and sphalerite. The largest specimen of the stalactitic type appears to have grown pendant from a projecting clump of marcasite, and on the massive form there is an incrustation of marcasite an inch in thickness.

In the denser parts of the specimen of the massive type the sphalerite is dull brown in color and the fracture has a fine-grained appearance. With a hand lens the intergrowths of galena can be seen, either in reticulated areas or single wavy fibers. In thin section, the galena fibers are occasionally branching, and in some places thicken up into masses. The fibers generally lie roughly parallel to the fissures in the sphalerite, but appear to be independent of the fissures and show no evidence of having been introduced along them. There does not seem to be any wurtzite in this part of the specimen. In the more open, spongy parts of the specimen there are numerous small pyramidal crystals of wurtzite, such as Rogers has described. Thin sections show the radial intergrowth of sphalerite and galena and areas of well-marked wurtzite. It is probable that the areas of wurtzite lie adjacent to the spongy cavities, but that can hardly be determined from the section, which went to pieces in the preparation.

The stalactitic specimens show stalactites from 2 to 6 or 8 millimeters in diameter, usually with a capillary tube in the center. Where the stalactites coalesce, they give rise to a massive stalactitic type. The stalactitic type very often develops into the botryoidal type. The radial intergrowths of galena and sphalerite are common, but some stalactites have little or no galena. No wurtzite was seen in the thin section of the stalactites, but it can be seen, macroscopically, in the crevices where adjoining stalactites come together. Smith, as noted above, says that some of the stalactites have a central core composed of galena. None of the typical round rodlike stalactites in the material at hand have a galena core, but there are two beautiful specimens of elongated forms of galena which are almost completely covered with a botryoidal incrustation of the radial sphalerite, which in turn is surmounted by perfect wurtzite pyramids as described by Rogers. Each specimen is likewise partly covered with marcasite, which is later than the sphalerite and apparently of the same age as the wurtzite, since wurtzite is found upon marcasite and marcasite upon wurtzite. The galena center in one specimen has the shape in cross section of a pointed Greek cross, and seems to be composed of four parallel elongated and flattened octahedral forms joined along a side edge. From each of the free edges, forming the pointed arms in cross section, there grows out a row of octahedral crystals of galena, much after the fashion described above by Chamberlin. In another specimen the galena center is a single strip representing an elongated and flattened cube 70 millimeters in length, 10 or 12 millimeters in width, and 3 millimeters in thickness.

Whether or not the stalactitic blende beneath wurtzite crystals is itself wurtzite, as thought by Rogers, it must nevertheless have been deposited from descending solutions and in an empty cavity, since under no other conditions can a stalactite be formed. Chamberlin[1] and Nason[2] both cite stalactites of pyrite, marcasite, galena, and sphalerite as proof of descending solutions and as deposited in cavities. If deposited by descending solutions the material of the stalactites must have been derived from the oxidation of the upper part of the ore body, and is therefore secondary and is a product of downward sulphide enrichment of more importance than those already noted. So far as known to the writer, this is the only occurrence of the ores in stalactitic form in the district. The peculiar intergrowth of galena and blende is, with the exception noted below, likewise peculiar to the Combination mine, as is also the occurrence of wurtzite crystals. As the wurtzite is younger than the secondary blende it is also probably secondary. In fact, Noelting[3] reached the conclusion, after extensive study of the occurrence of wurtzite from many localities, that it is invariably secondary. As was noted on page 246, the wurtzite in the Gagnon mine at Butte, Mont., in the Horn Silver mine, near Frisco, Utah, and at Tonopah, Nev., is believed to be secondary, deposited from descending acid sulphate solutions. The wurtzite in the Era district, Idaho, was deposited simultaneously with calcite, probably from solutions practically neutral, and is apparently of primary origin. This material and that from Joplin is all the wurtzite from America that has been thus far described. As already noted, the wurtzite at Joplin seems to be contemporaneous with the marcasite, with which it is intimately associated. This contemporaneity was to be expected, according to the results of the experiments made by Allen and associates, who, as outlined on page 243, obtained both marcasite and wurtzite from solutions acidified with strong acids. It would seem, then, that for some reason there was at this place a precipitation of zinc sulphide as wurtzite and of iron disulphide as marcasite from a descending solution containing free sulphuric acid. Elsewhere in the district, apparently, such descending solutions were for some reason unable to deposit wurtzite. In the experiments noted Allen was unable to produce wurtzite below 250° C. (480° F.). It is true that the oxidation of pyrite has been known to raise the temperature in mine drifts as high as 120° F., but it can hardly be supposed that the descending solutions in the combination ore body were at higher temperatures than those in adjacent ore bodies, or at anything like the high temperature indicated for the artificial formation of wurtzite.

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[1] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geology of Wisconsin, vol. 4, pp. 389-390, 1882.

[2] Nason, F. L., Am. Inst. Min. Eng. Trans., vol. 22, p. 642, 1894.

[3] Noelting, Johannes, Ueber das Verhältniss der sogenannten Schalenblende zur regulären Blende und zum hexagonalen Wurtzit, Inaug. Diss., p. 29, Kiel, 1887.

The explanation of this deposit probably lies in the nature of the normal ground water of the district, which is naturally a potable water, dominated by carbonates of the alkaline earths, for Haworth says[1] that "the well and spring waters before the mines were opened were first class, probably not surpassed in pleasantness of taste by any in the United States." The underground water table before mining began lay near the surface, and the country rock was largely limestone. Descending acid solutions, generated by the oxidizing sulphides, were probably almost always neutralized at once before the zinc in solution came into contact with a reducing agent.

W. George Waring has called the attention of the writer to a white deposit on coal and carbonaceous shale in the Old Shaft at the Oronogo Circle mine, at Oronogo, Mo., which seems to be the product of a reaction of the sort described. An analysis of the material shows the following constituents:

Analysis of white deposit on coal and carbonaceous shale, Oronogo, Mo.

[W. George Waring, analyst.]

$ZnCO_3$	84.08
$ZnSO_4$	12.74
H_2O (by difference)	3.18
	100.00

This deposit was apparently made by a solution containing zinc sulphate derived from the decomposition of zinc blende, the sulphate having been mostly changed to the carbonate, probably by reaction with calcium bicarbonate in the ground water. It will be noted that the deposit has been formed on carbonaceous material in an advantageous position for the reduction of zinc compounds, if carbonaceous matter in the form of coal can accomplish such reduction.

Water dripping from the roof of the sheet ground near the Wallace shaft of the Boston Get There tract, at Prosperity, Mo., forms, on the floor of the drift, a deposit which consists of zinc carbonate with traces of iron and a little lime. Qualitative analysis of the water, made in the chemical laboratory of the United States Geological Survey, shows that it contains calcium, sulphate, and carbonate in quantity; silica, 20 milligrams per liter, and zinc possibly 20 milligrams per liter, with a trace of lead. Probably here also a solution which, like the one noted above, originally containing zinc sulphate derived from the oxidation of sphalerite, has reacted with a calcium bicarbonate water.

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[1] Haworth, Erasmus, A contribution to the geology of the lead and zinc mining district of Cherokee County, Kans., p. 34, 1884.

Reactions such as these would undoubtedly be general in the zone of oxidation and in the upper portion of the ground water and would account for the lack of sulphide enrichment.

Pošepný [1] points out that sulphides are not formed in nature in the presence of air and therefore can not have been formed in the superficial zone or zone of oxidation, but must have been formed in depth. It is well known, of course, that sulphide and oxygen are chemically incompatible. Most secondary sulphides are deposited below water level. Although the upper part of the ground water may contain considerable available oxygen in the shape of dissolved air, or as free acids, Emmons [2] has shown that the quantity of free sulphuric acid, which is the significant acid in sulphide enrichment, rapidly decreases from the surface of the water downward, owing to the presence of neutralizing compounds in solution, in the gangue, or in the wall rock. Spencer [3] has shown that at Ely, Nev., the quantity of oxygen which rain water can hold in solution is not sufficient to have accomplished the oxidation which preceded the removal of the sulphides from the oxidized capping; hence he concludes that a large part of the oxygen came from the air that circulated in the capping. It is therefore conceivable that the descending currents of water and air may be so depleted of oxygen in the lower part of the superficial zone above the water level that precipitation of the sulphides can occur. Some such supposition as this is apparently necessary to account for the formation of the galena, sphalerite, and marcasite stalactites which have been reported from the upper Mississippi Valley region as well as from the Joplin region. Such a condition, however, seems to have been of very local occurrence in the Joplin region, and the sum total of enrichment by such sulphide deposition is inconsiderable.

Mr. R. S. Fitch called my attention to a pocket of ore on the 230-foot level in the Oronogo Circle mine, in which the sphalerite is of two generations. The first generation is of the ordinary variety with the usual cleavage and crystalline forms. This generation is bordered by crystals of chalcopyrite and beyond the chalcopyrite is an incrustation, a quarter of an inch thick, of dark blende, which has a wavy, somewhat radial cleavage. The incrustation, by filling in and around the crystals of the earlier generation, gives the whole a botryoidal shape. In thin section the incrusting portion is seen to be composed of an intimate undergrowth of galena and sphalerite of the same general character as that in the stalactitic ore from the Combination mine. In some places the intergrowth takes the form of parallel laths of galena and sphalerite; at other places there are smaller patches in which the lines of intergrowth run nearly at right angles to the lines in adjoining patches, giving a lattice-like effect somewhat like microcline twinning. Rarely a fiber of the sphalerite will appear to be doubly refracting, but this fact can hardly be taken to establish the presence of wurtzite; for, as Noelting[1] points out, sphalerite sometimes displays optical anomalies, though usually in thicker plates. As noted above, the specimen came from the 230-foot level. The lower limit of the oxidized zone in this mine lies at a depth of 75 or 80 feet. Between the oxidized zone and the 230-foot level ordinary sphalerite is found. It does not seem possible that the intergrowth of galena and blende here described, though resembling the secondary intergrowths from the Combination mine and though surmounting chalcopyrite and demonstrated to be a late generation, can be secondary; that is, derived from the zone of oxidation and deposited by descending waters, for the intervening 150 feet shows no evidences of secondary deposits. It is therefore concluded that this intergrown ore is primary but of a late generation.

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[1] Pošepný, Franz, Ueber die Entstehung der Blei-und Zinklagerstätten in auflöslichen Gesteinen: Berg- und Hüttenmännisches Jahrb., vol. 42, pp. 129–130, 1894.

[2] Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, pp. 89, 90, 1913.

[3] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, pp. 630–632, 1913.

CONCLUSION.

The writer is in complete accord with the following statements of Smith:[2]

> Aside from the small and unimportant amounts of sulphides unmistakably due to second concentration which have just been described, the recognition of sulphides deposited by descending waters is generally a difficult matter, both because they have been formed in the same way as the ores of first concentration—in the same place and by the same reducing agents—and because they occur merely as accretions to the older deposits. The difficulty is increased by the fact that, as pointed out by Van Hise and Bain, the ores of first concentration have continued to form ever since their deposition began and are probably still forming, so that additions to the deposits are being made by both ascending and descending waters. For this reason little can be determined by paragenesis, since different generations of ores might be equally well referred to either the ascending or the descending solutions. Furthermore, the later deposits are probably in many cases, if not usually, formed from a mingling of the two systems of waters, and where this is true, discrimination of the results is, of course, impossible. * * *
>
> In all instances noted by the writer where sulphide enrichment had apparently taken place, the amount of this enrichment, so far as it could be determined, was small as compared with the volume of the ores of first concentration, and generally of small economic importance. This is believed to be generally true for the district as a whole, although there may be a few ore bodies in which the ores of second concentration form an important part of the deposit near the lower limit of oxidation.

It can not be questioned that ore bodies within the zone of oxidation in the Joplin district are subject to oxidation and solution and are removed by those processes, a portion of the metals in solution being reprecipitated as sulphides. The present writer concludes that very little of the ore redeposited as sulphides can be recognized as having been transferred from the upper to the lower part of the same ore body, and that most of the material removed from an ore body during oxidation and redeposited as sulphides is transported and is added to other ore bodies, where it can not be distinguished from the minerals of primary deposition; and, accordingly, that recognizable downward sulphide enrichment in the Joplin district is negligible in quantity.

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[1] Noelting, Johannes, Ueber das Verhältniss der sogenannten Schalenblende zur regulären Blende und zum hexagonalen Wurtzit, Inaug.-Diss., p. 7, Kiel, 1887.

[2] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district, folio (No. 148), p. 19, 1907.

IMPOVERISHMENT.

That portion of an ore body in the zone of oxidation above water level is subject to decomposition and solution. In vein deposits, owing to the tendency of the vein walls to confine the flow, the material removed is most likely to be carried directly downward and, under suitable conditions, to be added to the lower part of the same ore body, resulting in enrichment. In other forms of deposits, however, the material may be transported laterally to a distance, in which event the original ore body is said to have suffered impoverishment. In the Joplin district the shallower "bunchy" or "broken ground" deposits, owing to the open character of the rocks, were peculiarly subject to this form of impoverishment during the weathering of the ore bodies.

Not only from the action of such descending waters did the ore bodies suffer impoverishment, but there are indications that ascending waters likewise caused impoverishment. In the sheet-ground deposits, which lie below the water table, galena and sphalerite are at many places etched, the sphalerite having a pitted to feathery surface and the galena having the octahedral faces truncating the cube deeply etched or corroded. The etching leaves the minerals bright and fresh looking and seems not to be due to oxidation. Specimens of galena from the Oronogo Mutual mine at Oronogo, Mo., which show this etching particularly well, came from the sheet ground at a depth of 170 feet below the level of Center Creek and 5 feet below any previous working. The galena had therefore always been below the permanent water level and below the water level established by pumping in that section. The specimens were furnished by W. George Waring, who states that the mine water is slightly alkaline.

In the mines at Miami, in both the shallow levels and the deep levels, some of the galena and sphalerite is etched and corroded. No oxidation whatever has taken place in these deposits, which have been protected from surface waters by a covering of Pennsylvanian shale and in which the water level stood at the surface until mining began. It seems certain that the etching of these minerals was due to the waters of the ascending artesian circulation, because there is good evidence (see pp. 203–205, 225–228) that the present mine waters are a part of the artesian circulation, and there is nothing to indicate that the ore bodies have ever been in the zone of oxidation since their segregation.

It is impossible to say absolutely that none of the removed material has been redeposited within the ore body, resulting in enrichment, but from the fact that the etching occurs in both the shallow and deep levels it is believed that there was little if any redeposition and that on the whole the action was that of impoverishment.

PRACTICAL BEARING OF THEORIES OF ORIGIN ON EXPLOITATION OF THE DEPOSITS.

IMPORTANCE OF THE SUBJECT.

The question of the genesis of the Joplin zinc and lead deposits is not merely of academic interest. On the contrary, it has a most practical bearing on prospecting and development work in the region and particularly on the broad selection of areas for prospecting. Practical application of deductions from the theories of descending solutions, laterally moving solutions, and ascending solutions will here be made to the actual or probable occurrence or nonoccurrence of ores in certain areas and under certain conditions. This will involve some repetition and restatement of facts scattered through the foregoing pages. It will be pointed out wherein it seems to the writer that some of the theories fail to explain certain conditions and how action on fair deductions from certain theories might lead to material losses in prospecting.

Ascending meteoric solutions heated by the intrusion of igneous bodies into sedimentary rocks must necessarily have derived the metals from the sedimentary rocks and have transported them by the artesian circulation. The effect of the heat would be to render the water more active. As it has already been shown that the artesian waters at normal temperatures are fully capable of taking the disseminated sulphides into solution, it is perhaps not necessary, in the absence of known intrusions in the mining region, to consider further the possibility of the influence of such intrusives on the artesian circulation. For identical reasons it is also probably not necessary to consider the alternative suggestion that magmatic waters dissolved metals from the sedimentary rocks and segregated them where they are now found.

OCCURRENCE OF ORE BENEATH MARGINAL PENNSYLVANIAN SHALE.

Smith [1] suggested the possibility of a belt of zinc and lead deposits in the area of Pennsylvanian rocks west of the known ore-bearing areas. This suggestion has been justified by the discovery of extensive ore bodies under the Pennsylvanian shale in the Miami district of Oklahoma and by their proved extension northward into Kansas under thicknesses of Pennsylvanian shale ranging from 50 or 60 to 300 feet. Under the artesian-circulation theory such deposits might naturally be expected in this position, the determining conditions being, first, suitable openings to receive the ores, and second, location not so far back beneath the shale as to be beyond the reach of the artesian circulation. The writer has on pages 34 and 205 suggested that the hydrostatic pressure of the outflowing artesian circulation forces a portion of the water forward beneath the inner margin of the Pennsylvanian shale, which results in a slow return flow toward the center of the uplift in the open ground just beneath the shale adjacent to its inner margin. This slow return flow in the open breccia ground favors the escape of carbon dioxide, and consequently the precipitation of the metals as sulphide by the hydrogen sulphide, and the writer believes that this part of the artesian circulation has been especially effective in the formation of the ores. It is plain that neither descending solutions nor laterally moving solutions could accomplish the segregation of ores in this position. Under these theories it would be considered useless to search for ore in such locations; whereas under the theory of ascending solutions this would be a prospective mining territory.

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[1] Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 16, 1907.

OCCURRENCE OF ORE ABOVE THE CHATTANOOGA SHALE.

No workable ore bodies have been found in the area extending from the vicinity of Granby, Mo., southeast to Fayetteville, Ark., and westward from this area to the border of the Pennsylvanian rocks in Oklahoma, which is known to be underlain by apparently persistent Chattanooga shale, as shown on Plate III. Under the theory of ascending solutions no ore was to be expected in this territory, as the ore-bearing artesian waters were prevented from ascending to the surface by the impervious shale. On the other hand, if the Boone furnished the metals, as postulated by the lateral secretion theory held by Schmidt and Winslow, or if the Pennsylvanian furnished the metals by descending solutions, as postulated by Buckley and Buehler, there is no apparent reason why the ores should not have been deposited throughout this region, for the Boone is the surface formation throughout this area, and the Pennsylvanian rocks formerly covered the whole region. Under the theories of descending or of laterally moving solutions this area would be prospective mining territory. Under the theory of ascending solutions ore would be looked for only in faults which permitted the ascent of solutions from below the shale. The Seneca fault is the only one known in this area, and ore deposits were found along its course from the northern margin of the Chattanooga shale to the point where the thickness of the shale was greater than the throw of the fault, and thus sealed it. If the ores were deposited by ascending solutions, therefore, it would probably be a waste of money to prospect in this area above the shale, except where there were evidences of faulting or some other reasons for believing that the shale beneath was not persistent.

OCCURRENCE OF ORE AT THE LEVEL OF THE CHATTANOOGA SHALE.

As pointed out in the body of this report, a systematic campaign of drilling was undertaken by the Granby Mining & Smelting Co. to develop a deep run of ore in the Granby district. The results of this drilling established the presence of a fairly persistent ore horizon at the level of the Chattanooga shale at a depth of about 300 feet, as shown on Plate IX. Buckley and Buehler pointed out in their report on the Granby area, which antedated the drilling, that if the ores have been deposited by ascending solutions they should occur plentifully at the horizon of the Chattanooga shale, where the solutions first came in contact with reducing material. The results of the drilling fully justify their reasoning. It remains to consider whether solutions moving directly downward from the surface could have formed these deposits. To whatever theory of ore deposition we may adhere, the fact of an artesian circulation in the Ozark uplift can not be denied. As shown on pages 33 to 37, the currents in the territory adjoining the retreating edge of the Pennsylvanian shale were ascending, especially at the places where the shale was first penetrated by erosion. The ore-bearing solutions can hardly be supposed to have diffused downward to the depth of the Chattanooga shale against these ascending currents. Directly descending solutions could hardly have reached such depths to deposit these ores unless the general underground water table had been lowered nearly to this level by the retreat, down the slope, of the inner edge of the Pennsylvanian. But experience in the Joplin region has shown that the water table in all new camps stood nearly at the surface of the ground or at least not lower than the surface drainage, and everything indicates that it stood so during the period of ore deposition.

OCCURRENCE OF ORE IN KINDERHOOK ROCKS.

In certain districts of the Joplin region the drill shows indications of ore rather widely distributed in the Kinderhook rocks in the lower part of the Boone formation. It has been recently proposed to prospect these rocks beneath a small structural basin shown on the structural map in the Joplin district geologic folio, on the supposition that descending waters would tend to be confined by the inclined limbs of the syncline and would deposit ores in the Kinderhook rocks in the lower part of the basin. For the reason already stated, it is not likely that descending solutions could have penetrated or diffused to such depths against the ascending currents, which must have existed, either to have deposited original ore bodies or to have enriched other deposits. On the other hand, there is no reason why the deposits might not have been formed in this location by ascending solutions if suitable openings existed and if physical conditions were right for their precipitation.

OCCURRENCE OF DEEP DEPOSITS OF ORE.

Lead and zinc ore has been mined at Aurora, Mo., in the eastern part of the Joplin district, at 320 feet in depth and is now being mined at that depth at Miami, Okla., in the extreme western part of the district. Indications of ore as strong as those usually regarded as justifying exploitation have frequently been found at greater depths than these in drilling in the district. Under the assumption of ascending solutions there is a chance that workable bodies of ore may be found at considerably greater depths than any heretofore worked. Under the theories of descending or laterally moving solutions it seems highly improbable that there are workable ore bodies at such depths.

POSSIBILITY OF IGNEOUS ORIGIN OF THE ORES.

In the foregoing discussion of the bearing of the theories of origin on practical field operations no distinction has been made between ascending artesian meteoric waters and ascending magmatic solutions. This report has been addressed to marshaling the evidence in favor of the origin of the ores from meteoric waters, and so, too, have almost all the reports dealing with the ores of the region, but the magmatic theory has not been without supporters. As already noted, an igneous origin for the ore deposits of the Ozark region was adopted by Jenney,[1] and has been advocated by Nason,[2] Wheeler,[3] Spurr,[4] Thomas,[5] and Pirsson,[6] although of these only Jenney has made detailed studies of the deposits.

Thomas suggested that the uplifting of the dome was possibly connected with the intrusion of igneous masses which may have supplied metal-bearing solutions. Pirsson thinks that the ore deposits may be related to intrusions, not yet uncovered by erosion, possibly of the general type of the mid-Cretaceous peridotite dikes and eleolite syenite intrusives of Arkansas or of the peridotite and lamprophyre dikes of western Kentucky and southern Illinois. Besides these intrusions in Arkansas, Kentucky, and Illinois there is the granite dike at Spavinaw, Okla., described by Drake[1] and the pegmatitic intrusion in Camden County, Mo., described by Winslow[2] and others, as well as the basic dikes in Ste. Genevieve County, Mo., which Buckley[3] says appear to have been intruded into the lower part of the Bonneterre formation. No ore deposits are associated even remotely with any of these intrusions, except those of southern Illinois and western Kentucky. The age of none of these intrusions is known except that of the peridotite dikes of Arkansas, which Miser[4] has shown to be mid-Cretaceous. Most of the intrusions are younger than the Carboniferous at least, and there is no evidence that they do not all date from the middle of Cretaceous time, which may fairly be presumed.

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[1] Jenny, W. P., Lead and zinc deposits of the Mississippi Valley: Am. Inst. Min. Eng. Trans., vol. 22, pp. 219–223, 1894.

[2] Nason, F. L., The disseminated lead ores of southeast Missouri: Eng. and Min. Jour., vol. 73, pp. 478–480, 1902.

[3] Wheeler, H. A., Notes on the source of the southeast Missouri lead: Eng. and Min. Jour., vol. 77, pp. 517–518, 1904.

[4] Spurr, J. E., A theory of ore deposition: Min. and Sci. Press, vol. 96, pp. 662–663, 1908.

[5] Thomas, Kirby, The Rand banket: Min. and Sci. Press, vol. 108, p. 226, 1914.

[6] Pirsson, L. V., Origin of certain ore deposits: Econ. Geology, vol. 10, pp. 180–186, 1915.

Nothing in the composition of the ores suggests that they were formed by hot waters. If formed by magmatic waters they must have traveled far enough from the parent igneous mass to have become cooled to normal ground-water temperatures. If formed by intrusions before the artesian circulation was initiated and while yet the Pennsylvanian shale covered the dome, the magmatic waters must have escaped upward through fractures in the sedimentary rocks, in which case we should expect the ore bodies to show some relation to the fractures. Though the ore bodies are closely related to solution channels, nothing comparable to fissure veins is to be noted. It seems unlikely, therefore, that the deposits can have been formed in this way. If formed by intrusions after the artesian circulation was established, the cooled magmatic waters probably mingled with the artesian waters. The location of any ore deposits from such mingled solutions would be determined by the artesian circulation, and there probably would be nothing in the form, composition, or location of the ores to distinguish those due to the magmatic water from those due to the meteoric water. Pirsson alludes to the fact of occurrence of the ores as evidence of igneous activity on the grounds that ore deposits are in general of igneous origin, but it is to be doubted whether this is available as evidence, since these deposits belong to a type the origin of which the world over has been constantly in dispute between the magmatists and the advocates of meteoric waters, the latter having perhaps the preponderance of numbers.

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[1] Drake, N. F., A geological reconnaissance of the coal fields of Indian Territory: Am. Philos. Soc. Proc., vol. 36, pp. 338-342, 1897.

[2] Winslow, Arthur, Lead and zinc deposits: Missouri Geol. Survey, vol. 7, pp. 432-434, 1894.

[3] Buckley, E. R., Lead and zinc deposits of the Ozark region: Types of ore deposits, p. 105, 1911.

[4] Miser, H. D., New areas of diamond-bearing peridotite in Arkansas: U. S. Geol. Survey Bull. 540, pp. 541-545, 1914.

The artesian-circulation theory starts with a proved ample source, connects that source with the iron, the lead, and the zinc deposits of the uplift through processes which can be observed in operation in the region, and offers in evidence the deposits themselves, which in location, form, composition, and gangue are in complete harmony with the theory.

The magmatic hypothesis can be put forward only as a possibility, as it starts with no proved source, it appeals to no process which can be recognized in operation in the region, and offers no single characteristic of the ore deposits which would be diagnostic of origin under the suggested process in contrast with the processes of the artesian circulation.

SUMMARY.

The theory that the Joplin ores were segregated from disseminated zinc and lead minerals in the Cambrian and Ordovician rocks of the Ozark uplift by artesian-circulating alkaline-saline sulphureted waters rests upon these facts, among others:

1. Since the Ozark dome was formed the circulation of the underground water in it has necessarily been artesian, the water flowing down the sides of the dome in the Cambrian, Ordovician, and overlying rocks and rising at the inner edge of the Pennsylvanian shale.

2. This circulating water is alkaline-saline, is dominated chemically by salts of the alkali metals, and holds in solution hydrogen sulphide and carbon dioxide—facts shown by analyses of the artesian waters rising from the Cambrian and Ordovician rocks on the slope of the dome, but especially by analyses of waters of wells reaching that horizon in the bordering Pennsylvanian area.

3. Waters of this character are competent to dissolve and transport the metals, as is shown by chemical experiment. Similar waters in other regions, notably in Kentucky, bring the metals to the surface, where, on the escape of the carbon dioxide, the dissolved metals are precipitated as sulphides by the hydrogen sulphide.

4. The waters of the Ozark artesian circulation rising from the Cambrian and Ordovician rocks are now dissolving the metals and bringing them to the surface, as is shown by analyses of such waters given herein and most conclusively by the presence of zinc and lead sulphides in the sediments deposited from such waters in reservoirs of waterworks and in other reservoirs.

5. The Cambrian and Ordovician limestones, as shown by analyses made by Robertson, contain zinc and lead in disseminated form and are a sufficient source of the metals.

6. The ratios of zinc to lead in the Cambrian and Ordovician limestones, in the reservoir sediments, and in the ores as mined are almost

identical, the metals of the sediments and the ores having been derived from the limestones according to the theory presented in this paper, whereas the ratios of zinc to lead in the crystalline rocks of the St. Francis Mountains and in the Mississippian rocks are decidedly different from the ratios in the Cambrian and Ordovician rocks as well as from each other.

7. The ratios of zinc to lead and to copper in the Cambrian and Ordovician rocks and the ratios of zinc to lead, copper, and iron in the ores and the sediments are in harmony with those required by the relative solubility of the mixed sulphides in contact, as determined by Gottschalk and Buehler, and by the relative ages of the deposits.

8. The ores of the different metals are disposed concentrically about the crystalline nucleus and about the center of the structural uplift, as demanded by Gottschalk and Buehler's results.

9. The Mississippian limestones adjacent to the ore deposits are largely dolomitized, whereas similar limestones in a similar position (except as to similar artesian circulation) in other districts than the Ozark region are not dolomitized. The Cambrian and Ordovician rocks are largely dolomites and magnesian limestones, and the waters drawn from that horizon are rich in magnesium.

The Mississippian limestones associated with the ore deposits are at some places completely silicified to chert or jasperoid, though at other places in the Mississippi Valley similar limestones, not associated with ore deposits, are not so silicified. The waters from the Cambrian and Ordovician rocks contain notable quantities of silica in solution.

If dolomite, jasperoid, and ore were carried up from the Cambrian and Ordovician by ascending currents their general association is easily understood. If they were brought down from above there is no apparent reason why there should not be dolomite or jasperoid in the limestones in other parts of the Mississippi Valley that were once overlain by Pennsylvanian rocks.

10. Where the unbroken continuity of the Chattanooga shale precludes the ascent of such solutions from the Cambrian and Ordovician rocks below, there are no deposits of ore, dolomite, or jasperoid in the overlying cherty limestones. Where, on the other hand, the shale is absent or its continuity is broken, as by the Seneca fault, there are deposits of ore, jasperoid, and dolomite. These facts demonstrate that the ores were deposited by ascending solutions and that these solutions rose from the Cambrian and Ordovician rocks.

11. Deep drilling in the Granby district has disclosed a practically persistent ore horizon at the level of the Chattanooga shale or immediately beneath it, which is to be expected if the ore solutions came from below the shale, but not if they came from above it.

12. The mining areas lie in a practically continuous belt (except the area underlain by unbroken Chattanooga shale) around the inner margin of the Pennsylvanian rocks, an arrangement most easily explained by postulating deposition from ascending artesian water at the inner edge of the Pennsylvanian rocks.

13. The deep-lying deposits of zinc and lead that have been struck in drilling in the Joplin district and elsewhere occur at depths that could be reached only by meteoric waters having artesian circulation.

14. The mine waters at Miami, Okla., the only mines beneath the unbroken Pennsylvanian shale and hence presumably the only mine waters truly representing the ore-depositing solutions, are the only sulphureted mine waters in the district, and, in the synoptical table here presented (pp. 149, 150) fall alongside the water from the deep wells at Miami, Okla., and Clinton, Mo. The water from the Church mine showed, on analysis, a trace of zinc.

15. The occurrence of ore at the base of the Pennsylvanian rocks in places where, as at Miami, Okla., the rocks are not cut through by erosion, implies deposition by ascending waters.

16. The occurrence of bitumen associated with the ores at the base of the Pennsylvanian rocks is incontrovertible evidence that the solutions bearing the hydrocarbon that was fractionated by the shale were ascending.

17. Lead and zinc deposits of greater or less economic importance are associated with all geanticlinal uplifts and some of the marginal slopes of the Mississippi Valley—that is to say, they occur in regions affording artesian circulation of ground water.

18. Lead, zinc, copper, and iron are precipitated from the deep-well waters of the Ozark region on standing, as a result of the escape of carbon dioxide. The ore deposits of the Joplin region occur typically in breccias. Breccias favor the adsorption of the metallic salts and the escape of the gases in ascending solutions, but would not have the same effect on descending solutions. Therefore, the occurrence of the ores in breccias in the Joplin region indicates deposition by ascending solutions.

19. In the Miami district, where very little surface water enters the mines, the quantity of water necessary to be pumped to keep the underground water table down to a particular level is remarkably constant, being entirely free from seasonal variations. However, as mining has grown deeper and more extended, the quantity of water to be raised has steadily increased to more than treble its original quantity. This water is charged with hydrogen sulphide and otherwise closely resembles the deep-well waters, but it differs greatly from surface water. It is therefore probably a deep water which has ascended from the Cambrian and Ordovician rocks under artesian pressure, and it is probably similar to the solutions that deposited

the ores. So also there must be a constant deep-seated increment to the mine waters of all the mining districts of the Joplin region, though this increment may be almost completely masked by the seasonal variations.

20. Calculations based on the large-quantity analyses of the Cambrian and Ordovician rocks of the Ozark dome show that they contain more than 1,000 times as much zinc as is estimated to have been contained in the minable and unminable ore bodies of the dome. The zinc content of the pore water in the Cambrian and Ordovician rocks of the dome is one-thirteenth that of the estimated ore bodies of the dome. The pore water would have to be completely changed 13 times to transport the metals of the ore bodies. The original pore water of the dome probably had approximately the composition of sea water. If sea water is diluted to twice its volume 13 times in succession the solution will have only $\frac{1}{8192}$ of its original salinity. On comparing the saline content of sea water divided by 8192 with the average saline content of the water of a number of wells about Joplin it is found that the well waters contain nine times as much of the alkali metals and three times as much chlorine. The excesses in alkaline earths and sulphate are much greater, but they are obviously contributed by the surface waters added to the artesian circulation. The close agreement of the alkalies and the chlorine with the theoretical dilution indicates that the ground water has changed just about the number of times necessary to transport the metals of the ore deposits.

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  - *See also* Carbonates; Metals; Sphalerite; Sulphates; Sulphides; Sulphozincates; Waters, zinc-bearing; *and* Zincates.
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  - transfer of zinc as 51-52

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